ON THE ANHARMONIC, MULTI-PHONON, DEBYE-WALLER CONTRIBUTIONS TO THE PHONON-LIMITED RESISTIVITY OF METALS: APPLICATIONS TO Na AND K

by

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A Thesis

submitted to the Department of Physics

in partial fulfilment of the requirements

for the degree of

Master of Science

July 1979

Brock University

St. Catharines, Ontario

To Audrey

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ABSTRACT

The anharmonic, multi-phonon (MP), and Debye-Waller factor (DW) contributions to the phonon limited resistivity (ρ) of metals derived by Shukla and Muller (1979) by the doubletime temperature dependent Green function method have been numerically evaluated for Na and K in the high temperature limit. The anharmonic contributions arise from the cubic and quartic shift of phonons (CS, QS), and phonon width (W) and the interference term (I). The QS, MP and DW contributions to ρ are also derived by the matrix element method and the results are in agreement with those of Shukla and Muller (1979). In the high temperature limit, the contributions to ρ from each of the above mentioned terms are of the type BT^2. For numerical calculations suitable expressions are derived for the anharmonic contributions to ρ in terms of the third and fourth rank tensors obtained by the Ewald procedure. The numerical calculation of the contributions to ρ from the DW, MP term and the QS have been done exactly and from the CS, W and I terms only approximately in the partial and total Einstein approximations (PEA, TEA), using a first principle approach (Shukla and Taylor (1976)). The results obtained indicate that there is a strong pairwise cancellation between the: DW and MP terms, the QS and CS and the W and I terms.

The sum total of these contributions to ρ for Na and K amounts to 4 to 11% and 2 to 7%, respectively, in the PEA while in the TEA they amount to 3 to 7% and 1 to 4%, respectively, in the temperature range Θ_D to T_M.

ACKNOWLEDGEMENTS

The analytical and numerical calculations presented in this thesis were suggested and supervised by Dr. R. C. Shukla. I would like to express my gratitude to him for his constant encouragement and personal help.

I would also like to thank the Province of Ontario for the award of an Ontario Graduate Scholarship, the Natural Science and Engineering Research Council of Canada, and the Department of Physics of Brock University for their financial assistance.

Lastly, I would like to express my appreciation to Miss J. Hastie for typing this manuscript and to Brock University Computer Centre for their excellent services throughout the course of this work.

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1. INTRODUCTION

In a crystal lattice when the electrons are subjected to an electrical field in a given direction, they continue to move in that direction indefinitely without being deviated from their path until they suffer some kind of scattering. This causes the electrical resistance in metals. Some of the possible causes of electron scattering are:

a) the displacement of the ions from their equilibrium position due to the thermal motion

b) other electrons

c) lattice defects.

The dominant contribution to the electrical resistivity (ρ) at high temperature is the scattering of the electrons from the thermal motion of the ions. The quanta of energy from the thermal motion of the ions are called phonons. In order to calculate the scattering of the electrons from the ions we need to know the electron-ion interaction or in other words the electron-phonon matrix element. The phonons for a mode $\underset{\sim}{q}j$ are characterized by their eigenvalues ($\omega_{\underset{\sim}{q}j}$) and eigenvectors ($\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}$), where $\underset{\sim}{q}$ is the wave vector and j is the branch index.

Probably the first rigorous formulation of the electron-phonon matrix element was done by Bardeen (1937) where he extended the rigid ion model of Nordheim (1931) to take into account the shift in the charge density of the conduction electrons. This shift was taken into account by expressing the electron-phonon matrix element in terms of the bare electron ion matrix element divided by the dielectric constant of the electron gas. This is called the form factor $W(|\underset{\sim}{q}|)$. The essential ingredients in the calculation of ρ are the $\omega_{\underset{\sim}{q}j}$ and the associated $\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}$ for a phonon of mode ($\underset{\sim}{q}j$) and the form factor, $W\ (|q|)$.

All the previous calculations of ρ such as those of Darby and March (1964), Greene and Kohn (1965), Dynes and Carbotte (1968), Hayman and Carbotte (1971), and Kaveh and Wiser (1974) have employed a parametric representation of $W(|\underset{\sim}{q}|)$ and $(\omega_{\underset{\sim}{q}j}, \underset{\sim}{\epsilon}_{\underset{\sim}{q}j})$ with the parameters adjusted to fit experiment. In their calculations they used the Born-von Karman model. The force constants of this model are obtained from the nonlinear least square fit of the phonon dispersion curves measured along the three principal symmetry directions of the crystal by the inelastic neutron scattering experiments.

The $(\omega_{\underset{\sim}{q}j}, \epsilon_{\underset{\sim}{q}j})$ are then calculated from the Born-von Karman fit for any wave vector $\underset{\sim}{q}$ in the first Brillouin zone (F.B.Z.). The form factor $W(|\underset{\sim}{q}|)$ in all of the above calculations was taken to be a simple function of one or two parameters which were adjusted to fit the experimental value of ρ at some temperature . The two adjustable parameters in $W(|\underset{\sim}{q}|)$ in the calculation of Greene and Kohn (1965) were determined from the phase shift analysis. Dynes and Carbotte (1968) employed the Heine-Abarenkov form of $W(|\underset{\sim}{q}|)$. Hayman and Carbotte (1971) did their calculations with the help of Ashcroft-pseudopotential form factor $W(|\underset{\sim}{q}|)$ with one adjustable parameter. Kaveh and Wiser (1974) represented $W(|\underset{\sim}{q}|)$ by a one parameter model potential.

In all of the above calculations relatively good agreement was obtained with the experimental values of ρ. In spite of the success of these calculations we first note that all of them used the Lindhard (1954) screening function which gives a negative pair distribution function and does not satisfy the compressibility sum rule. The second point we note (for the sake of consistency) that the phonon frequencies $\omega_{\underset{\sim}{q}j}$ and the associated eigenvectors $\epsilon_{\underset{\sim}{q}j}$ must be obtained from the same form factor. In the above calculations $\omega_{\underset{\sim}{q}j}$ and $\underset{\sim}{\epsilon}_{\underset{\sim}{q}j}$ are totally unrelated to the form factor used in the calculation of ρ. In calculations of this kind it is not too surprising to obtain good agreement with the experiment since so many adjustable parameters have been fitted to the different existing experimental information. Thus a more meaningful theoretical calculation would be the one from first principles with no adjustable parameters fitted to any experimental results.

Such a first principle calculation has been done by Shukla and Taylor (1975) for Na and K in the temperature range 20^{0}K to melting based on the formula (2.1). They have used $W(|\underset{\sim}{q}|)$ obtained by Rasolt and Taylor (1975) from the theoretical calculations of Dagens et al (1975) with no adjustable parameters fitted to the experimental values of ρ. Also $\omega_{\underset{\sim}{q}j}$ and $\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}$ were obtained from the same $W(|\underset{\sim}{q}|)$. The screening function used by them was taken from Geldart and Taylor (1970) which has none of the problems associated with it as does the Lindhard screening function. The agreement between the calculated and measured values of ρ for K was better than 3% for all $T \geq 40^{0}$K and for Na better than 4% for all $T \geq 60^{0}$K. This would indicate that any correction to ρ in the high temperature limit from other sources (such as the phonon-phonon scattering) would be small.

In a recent paper Grimvall (1973) has analysed the experimental data of ρ for Na and K obtained by Dugdale and Gugan (1960, 1962). In his analysis of ρ he first reduced the experimental data for ρ to that at 0^{0}K volume and then subtracted the estimated contribution to ρ from the lattice defects (vacancies). He then plotted ρ/T as a function of $1/T^2$ and assumed that if it were not for the correction from some other type of scattering the points would asymptotically approach a straight line for high temperatures. The asymptote was obtained from the Bloch-Gruneisen formula based on the assumption that the correction to ρ from other types of scattering was zero for $T < \Theta_D$, where Θ_D is the Debye temperature.

From this analysis Grimvall (1973) concluded that the usual formula for ρ (see Sec. 2) overestimated the temperature dependence of the $0^{o}K$ volume resistivity in the high temperature limit by the $\sim$10% and the possible corrections for $T > \Theta_D$ to ρ would be of the form BT^2, where B is some constant. Grimvall (1973) surmised that the extra sources of scattering may be coming from such effects as the Debye-Waller factor, multi-phonon series and lattice anharmonicity. However, no attempt was made by him to derive the contributions to ρ from these scattering processes.

The theoretical findings of Shukla and Taylor (1975) and the semi-empirical analysis of Grimvall (1973) are in sharp contrast and raises the question "Is the BT^2 type of correction indeed of the order of 10%?" To answer this question one first has to derive all the contributions to the coefficient B from the various scattering processes.

These contributions have been enumerated in a recent paper by Shukla, Muller, and VanderSchans (1978). They arise from the Debye-Waller factor (DW), the first term of the multi-phonon series (MP) and the terms from the lattice anharmonicity such as the cubic shift (CS), quartic shift (QS), width (W) and the interference term (I).

It would be of some interest to calculate these contributions from the same first principle approach as used by Shukla and Taylor (1975). This is one of the objectives of this thesis.

The outline of this thesis is as follows:

In Sec. 2 we present the derivation of $S(\underset{\sim}{q},\omega)$ arising from the harmonic and the simplest anharmonic term in the Hamiltonian (viz.,QS) as well as the MP and DW contributions to $S(\underset{\sim}{q},\omega)$. The derivation is carried out by the straight forward calculation of the matrix elements. The corresponding contributions to ρ are derived and presented in Sec. 3.

This approach becomes very tedious in the derivation of the remaining contributions to $S(\underset{\sim}{q},\omega)$ arising from the cubic shift and width of phonons (CS, WD) and the interference term (I) and the contributions to ρ from these processes are summarized in Sec. 3 from the results of Shukla and Muller (1979). They have derived these contributions from the double-time temperature dependent Green function method. Sec. 4 contains the expressions for the contributions to ρ in the high temperature limit. In Sec. 5 we describe the numerical calculations for all the processes described above to obtain the T^2 contributions to ρ. These results are discussed in Sec. 6 and finally the conclusions of this thesis are presented in Sec. 7.

2.0 THEORY

Bhatia and Krishnan (1948) and later on many authors [Ziman (1960), Baym (1964), Greene and Kohn (1965), Dynes and Carbotte (1968)] have derived from the Boltzmann equation the following formula for the electrical resistivity (ρ) of simple metals with spherical Fermi surface.

$$\rho(T) = C' \sum_j \int_{<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|\, |W(|\underset{\sim}{q}|)|^2 |\underset{\sim}{q} \cdot \underset{\sim}{\hat{\epsilon}}_{qj}|^2 f(\beta\hbar\omega_{\underset{\sim}{q}j}) \quad (2.1)$$

where

$$f(\beta\hbar\omega_{\underset{\sim}{q}j}) = \left[e^{\beta\hbar\omega_{\underset{\sim}{q}j}} - 1\right]\left[1 - e^{\beta\hbar\omega_{\underset{\sim}{q}j}}\right]$$

In the above equation $W(|\underset{\sim}{q}|)$ represents the screened electron-ion pseudo-potential form factor and $\omega_{\underset{\sim}{q}j}$ and $\hat{\epsilon}_{\underset{\sim}{q}j}$ are the phonon frequencies and associated eigen vectors for the mode $\underset{\sim}{q}j$. The integration over the wave vector $\underset{\sim}{q}$ extends beyond the first Brillouin zone (F,B,Z.) out to a sphere of radius $2k_F$. The other constants are given by $\beta = (k_BT)^{-1}$ where k_B is the Boltzmann constant, T is the absolute temperature, and

$$C' = \frac{3\hbar\Omega_0}{16Me^2v_F^2k_F^2}$$

where $\hbar$ is the Planck's constant divided by 2π, Ω_0 is the volume per ion, M is the ion mass, v_F the Fermi velocity, e the charge of the electron, and K_F is the Fermi radius.

Baym (1964) and Greene and Kohn (1965) derived the above expression from the following general expression of ρ(T), viz.,

$$\rho(T) = c \int_{<2k_F} d^3q \, |\underset{\sim}{q}| \, |W(|\underset{\sim}{q}|)|^2 \int_{-\infty}^{+\infty} d\omega \, S(\underset{\sim}{q},\omega) \frac{\beta\omega}{(e^{\beta\hbar\omega}-1)} \tag{2.2}$$

where $c = \frac{M}{\hbar} c'$

and
$$S(\underset{\sim}{q},\omega) = \frac{1}{2\pi N} \int_{-\infty}^{+\infty} dt \, e^{i\omega t} \Big\langle \sum_{\ell\ell'} e^{-i\underset{\sim}{q}\cdot\underset{\sim}{X}_\ell(t)} \times e^{i\underset{\sim}{q}\cdot\underset{\sim}{X}_{\ell'}(0)} \Big\rangle \tag{2.3}$$

In Eq. (2.3) $\underset{\sim}{X}_\ell(0)$ and $\underset{\sim}{X}_\ell(t)$ represent the instantaneous position of the ℓ^{th} ion at time t and t = 0 respectively, and the angular bracket denotes the thermal average defined by

$$\langle O \rangle = \frac{Tr \, e^{-\beta H} O}{Tr \, e^{-\beta H}} \tag{2.4}$$

where in Eq. (2.4) Tr denotes the trace of the operator and implies the summation of diagonal elements in the matrix representation of the operator, and H is the Hamiltonian of the system.

If in Eq. (2.3) and (2.4), H is replaced by H_0 (the harmonic Hamiltonian), one obtains the usual resistivity formula (2.1). However, as pointed out in the introduction, we shall go beyond the harmonic approximation to obtain the T^2 term in the high temperature limit in the resistivity formula. We use the following H in Eq. (2.4), viz.

$$H = H_0 + H_A \tag{2.5}$$

where H_o and H_A represent the harmonic and anharmonic components of H and their explicit representation in the second quantized form is given by:

$$H_o = \sum_{\underset{\sim}{q}j} \hbar \omega_{\underset{\sim}{q}j} (a^{+}_{\underset{\sim}{q}j} a_{\underset{\sim}{q}j} + \frac{1}{2}) \tag{2.5a}$$

$$H_A = \sum_{\substack{q_1 q_2 q_3 \\ j_1 j_2 j_3}} V^3(\underset{\sim}{q}_1 j_1, \underset{\sim}{q}_2 j_2, \underset{\sim}{q}_3 j_3) A_{\underset{\sim}{q}_1 j_1} A_{\underset{\sim}{q}_2 j_2} A_{\underset{\sim}{q}_3 j_3}$$

$$+ \sum_{\substack{q_1 q_2 q_3 q_4 \\ j_1 j_2 j_3 j_4}} V^4(\underset{\sim}{q}_1 j_1, \underset{\sim}{q}_2 j_2, \underset{\sim}{q}_3 j_3, \underset{\sim}{q}_4 j_4) A_{\underset{\sim}{q}_1 j_1} A_{\underset{\sim}{q}_2 j_2} A_{\underset{\sim}{q}_3 j_3} A_{\underset{\sim}{q}_4 j_4} \tag{2.5b}$$

The various symbols appearing in Eq. (2.5) are defined as follows: a^{+}_{qj} and a_{qj} are the phonon creation and annihilation operators, $A_{\underset{\sim}{q}j} = a^{+}_{-\underset{\sim}{q}j} + a_{\underset{\sim}{q}j}$, $A_{-\underset{\sim}{q}j} = a^{+}_{\underset{\sim}{q}j} + a_{-\underset{\sim}{q}j} = A^{+}_{\underset{\sim}{q}j}$, $V^3(\underset{\sim}{q}_1 j_1, \underset{\sim}{q}_2 j_2, \underset{\sim}{q}_3 j_3)$ and $V^4(\underset{\sim}{q}_1 j_1, \underset{\sim}{q}_2 j_2, \underset{\sim}{q}_3 j_3, \underset{\sim}{q}_4 j_4)$ are the Fourier transforms of the anharmonic force constants defined explicitly by Shukla and Muller (1971) and Born and Huang (1954).

Since we are interested in the dynamical motion of the ions (characterized by the displacement $\underset{\sim}{u}_\ell(t)$ and not in their equilibrium positions $\underset{\sim}{R}_\ell(0)$) from the viewpoint of the resistivity calculation, we separate these parts in Eq. (2.3). Substituting,

$$\underset{\sim}{X}_\ell(t) = \underset{\sim}{R}_\ell(0) + \underset{\sim}{u}_\ell(t)$$

and noting that $\underset{\sim}{R}_\ell(0)$ and $\underset{\sim}{u}_\ell(t)$ commute because $\underset{\sim}{R}_\ell(0)$ is a c-number and $\underset{\sim}{u}_\ell(t)$ is the operator or a q number, we obtain for $S(\underset{\sim}{q},\omega)$

$$S(\underset{\sim}{q},\omega) = \frac{1}{2\pi N} \int_{-\infty}^{+\infty} e^{i\omega t} \sum_{\ell\ell'} e^{-i\underset{\sim}{q}\cdot(\underset{\sim}{R}_\ell(0) - \underset{\sim}{R}_{\ell'}(0))}$$

$$\times \left\langle e^{-i\underset{\sim}{q}\cdot\underset{\sim}{u}_\ell(t)} \, e^{i\underset{\sim}{q}\cdot\underset{\sim}{u}_{\ell'}(0)} \right\rangle dt \tag{2.6}$$

Expanding the product of exponentials in Eq. (2.6) and recalling that the operators $\underset{\sim}{u}_\ell(t)$ and $\underset{\sim}{u}_\ell(0)$ do not commute, we obtain the following expansion to $O(\underset{\sim}{u}_\ell^4)$, viz.,

$$\begin{aligned}
e^{-i\underset{\sim}{q}\cdot\underset{\sim}{u}_\ell(t)}\, e^{i\underset{\sim}{q}\cdot\underset{\sim}{u}_{\ell'}(0)} &= 1 + (-i\underset{\sim}{q}\cdot\underset{\sim}{u}_\ell(t) + i\underset{\sim}{q}\cdot\underset{\sim}{u}_{\ell'}(0)) \\
&+ \left[\frac{1}{2!}(-i\underset{\sim}{q}\cdot\underset{\sim}{u}_\ell(t))^2 + \frac{1}{2!}(i\underset{\sim}{q}\cdot\underset{\sim}{u}_{\ell'}(0))^2 + (-i\underset{\sim}{q}\cdot\underset{\sim}{u}_\ell(t))(i\underset{\sim}{q}\cdot\underset{\sim}{u}_{\ell'}(0))\right] \\
&+ \left[\frac{1}{3!}(-i\underset{\sim}{q}\cdot\underset{\sim}{u}_\ell(t))^3 + \frac{1}{3!}(i\underset{\sim}{q}\cdot\underset{\sim}{u}_{\ell'}(0))^3 + \frac{1}{2!}(-i\underset{\sim}{q}\cdot\underset{\sim}{u}_\ell(t))^2(i\underset{\sim}{q}\cdot\underset{\sim}{u}_{\ell'}(0))\right. \\
&\left. + \frac{1}{2!}(-i\underset{\sim}{q}\cdot\underset{\sim}{u}_\ell(t))(i\underset{\sim}{q}\cdot\underset{\sim}{u}_{\ell'}(0))^2\right] + \left[\frac{1}{4!}(-i\underset{\sim}{q}\cdot\underset{\sim}{u}_\ell(t))^4 + \frac{1}{4!}(i\underset{\sim}{q}\cdot\underset{\sim}{u}_{\ell'}(0))^4\right. \\
&+ \frac{1}{3!}(-i\underset{\sim}{q}\cdot\underset{\sim}{u}_\ell(t))^3(i\underset{\sim}{q}\cdot\underset{\sim}{u}_{\ell'}(0)) + \frac{1}{3!}(-i\underset{\sim}{q}\cdot\underset{\sim}{u}_\ell(t))(i\underset{\sim}{q}\cdot\underset{\sim}{u}_{\ell'}(0))^3 \\
&\left. + \left(\frac{1}{2!}\right)^2(-i\underset{\sim}{q}\cdot\underset{\sim}{u}_\ell(t))^2(i\underset{\sim}{q}\cdot\underset{\sim}{u}_{\ell'}(0))^2\right] + \cdots \qquad (2.7)
\end{aligned}$$

When Eq. (2.7) is averaged with respect to the Hamiltonian H defined by Eq. (2.5), all equal time odd power displacement terms vanish, as shown by Shukla and Muller (1970). Hence we drop these terms in the subsequent calculations of $S(\underset{\sim}{q},\omega)$.

Substituting Eq. (2.7) into Eq. (2.6), we obtain

$$S(\underset{\sim}{q},\omega) = S_0(\underset{\sim}{q},\omega) + S_2(\underset{\sim}{q},\omega) + S_3(\underset{\sim}{q},\omega) + S_4(\underset{\sim}{q},\omega)$$

where $S_0(\underset{\sim}{q},\omega)$ is the elastic contribution to $S(\underset{\sim}{q},\omega)$ which arises from the equal time correlation function of the displacement terms in Eq. (2.7).

This is of no interest in the calculation of ρ and hence we omit $S_0(\underset{\sim}{q},\omega)$ in the subsequent calculations. $S_2(\underset{\sim}{q},\omega)$, $S_3(\underset{\sim}{q},\omega)$ and $S_4(\underset{\sim}{q},\omega)$ represent the contributions from the 2, 3 and 4 displacement operators respectively. Explicitly these terms are given by

$$S_2(\underset{\sim}{q},\omega) = \frac{1}{2\pi N}\int_{-\infty}^{+\infty} dt\, e^{i\omega t} \sum_{\ell\ell'} e^{-i\underset{\sim}{q}\cdot(\underset{\sim}{R}_\ell(0)-\underset{\sim}{R}_{\ell'}(0))}$$

$$\times \left\langle (-i\underset{\sim}{q}\cdot\underset{\sim}{u}_\ell(t))(i\underset{\sim}{q}\cdot\underset{\sim}{u}_{\ell'}(0)) \right\rangle \qquad (2.8)$$

$$S_3(\underset{\sim}{q},\omega) = \frac{1}{2\pi N}\int_{-\infty}^{+\infty} dt\, e^{i\omega t} \sum_{\ell\ell'} e^{-i\underset{\sim}{q}\cdot(\underset{\sim}{R}_\ell(0)-\underset{\sim}{R}_{\ell'}(0))}$$

$$\times \left[\frac{1}{2!}\left\langle (-i\underset{\sim}{q}\cdot\underset{\sim}{u}_\ell(t))^2(i\underset{\sim}{q}\cdot\underset{\sim}{u}_{\ell'}(0)) \right\rangle \right.$$

$$\left. + \frac{1}{2!}\left\langle (-i\underset{\sim}{q}\cdot\underset{\sim}{u}_\ell(t))(i\underset{\sim}{q}\cdot\underset{\sim}{u}_{\ell'}(0))^2 \right\rangle \right] \qquad (2.9)$$

and

$$S_4(\underset{\sim}{q},\omega) = \frac{1}{2\pi N}\int_{-\infty}^{+\infty} dt\, e^{i\omega t} \sum_{\ell\ell'} e^{-i\underset{\sim}{q}\cdot(\underset{\sim}{R}_\ell(0)-\underset{\sim}{R}_{\ell'}(0))}$$

$$\times \left[\frac{1}{3!}\left\langle (-i\underset{\sim}{q}\cdot\underset{\sim}{u}_\ell(t))^3(i\underset{\sim}{q}\cdot\underset{\sim}{u}_{\ell'}(0)) \right\rangle \right.$$

$$+ \frac{1}{3!}\left\langle (-i\underset{\sim}{q}\cdot\underset{\sim}{u}_\ell(t))(i\underset{\sim}{q}\cdot\underset{\sim}{u}_{\ell'}(0))^3 \right\rangle$$

$$\left. + \left(\frac{1}{2!}\right)^2\left\langle (-i\underset{\sim}{q}\cdot\underset{\sim}{u}_\ell(t))^2(i\underset{\sim}{q}\cdot\underset{\sim}{u}_{\ell'}(0))^2 \right\rangle \right] \qquad (2.10)$$

The ℓ sums in Eqs. (2.8), (2.9) and (2.10) can be eliminated by the following Fourier representation of $\underset{\sim}{u}_\ell(t)$

$$\underset{\sim}{u}_\ell(t) = \left(\frac{\hbar}{2MN}\right)^{1/2} \sum_{\underset{\sim}{q}j} \frac{\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}}{(\omega_{\underset{\sim}{q}j})^{1/2}} e^{i\underset{\sim}{q}\cdot\underset{\sim}{R}_\ell(0)} A_{\underset{\sim}{q}j}(t) \qquad (2.11)$$

where $A_{\underset{\sim}{q}j}(t)$ in Eq. (2.11) is defined in the Heinsberg representation, viz.,

$$A_{\underset{\sim}{q}j}(t) = e^{iHt/\hbar} A_{\underset{\sim}{q}j}(0)\, e^{-iHt/\hbar}$$

Substituting for $\underset{\sim}{u}_\ell(t)$ from Eq (2.11) into Eqs. (2.8), (2.9) and (2.10) and then interchanging the B.Z. sums over $\underset{\sim}{q}$ with the direct lattice sums over ℓ and employing the lattice sum

$$\sum_\ell e^{i\underset{\sim}{Q}\cdot\underset{\sim}{R}_\ell(0)} = N\Delta(\underset{\sim}{Q}+\underset{\sim}{\tau})$$

where N is the number of unit cells, $\underset{\sim}{\tau}$ is a vector of the reciprocal lattice, and $\Delta(\underset{\sim}{Q}+\underset{\sim}{\tau})$ is the delta function, we obtain

$$S_2(\underset{\sim}{q},\omega) = N\left(\frac{\hbar}{2MN}\right) \sum_{\substack{q_1 q_2\\ j_1 j_2}} \Delta(-\underset{\sim}{q}+\underset{\sim}{q}_1)\Delta(\underset{\sim}{q}+\underset{\sim}{q}_2)$$

$$\times \frac{(\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{q_1 j_1})(\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{q_2 j_2})}{(\omega_{q_1 j_1}\,\omega_{q_2 j_2})^{1/2}} J_2 \qquad (2.12)$$

$$S_3(\underset{\sim}{q},\omega) = S_3^A(\underset{\sim}{q},\omega) + S_3^B(\underset{\sim}{q},\omega)$$

and $$S_4(\underset{\sim}{q},\omega) = S_4^A(\underset{\sim}{q},\omega) + S_4^B(\underset{\sim}{q},\omega) + S_4^C(\underset{\sim}{q},\omega)$$

where

$$S_3^A(\underset{\sim}{q},\omega) = -\sum_{\substack{q_1 q_2 q_3\\ j_1 j_2 j_3}} f^3(\underset{\sim}{q}_1 j_1, \underset{\sim}{q}_2 j_2, \underset{\sim}{q}_3 j_3)\,\Delta(-\underset{\sim}{q}+\underset{\sim}{q}_1+\underset{\sim}{q}_2)$$

$$\times \Delta(\underset{\sim}{q}+\underset{\sim}{q}_3)\, J_3^A \qquad (2.13)$$

$$S_3^B(\underset{\sim}{q},\omega) = \sum_{\substack{\underset{\sim}{q}_1 \underset{\sim}{q}_2 \underset{\sim}{q}_3 \\ j_1 j_2 j_3}} f^3(\underset{\sim}{q}_1 j_1, \underset{\sim}{q}_2 j_2, \underset{\sim}{q}_3 j_3)\, \Delta(-\underset{\sim}{q}+\underset{\sim}{q}_1)$$

$$\times\, \Delta(\underset{\sim}{q}+\underset{\sim}{q}_2+\underset{\sim}{q}_3)\, J_3^B \tag{2.14}$$

$$S_4^A(\underset{\sim}{q},\omega) = \frac{1}{3!} \sum_{\substack{\underset{\sim}{q}_1 \underset{\sim}{q}_2 \underset{\sim}{q}_3 \underset{\sim}{q}_4 \\ j_1 j_2 j_3 j_4}} f^4(\underset{\sim}{q}_1 j_1, \underset{\sim}{q}_2 j_2, \underset{\sim}{q}_3 j_3, \underset{\sim}{q}_4 j_4)$$

$$\times\, \Delta(-\underset{\sim}{q}+\underset{\sim}{q}_1+\underset{\sim}{q}_2+\underset{\sim}{q}_3)\, \Delta(\underset{\sim}{q}+\underset{\sim}{q}_4)\, J_4^A \tag{2.15}$$

$$S_4^B(\underset{\sim}{q},\omega) = \frac{1}{3!} \sum_{\substack{\underset{\sim}{q}_1 \underset{\sim}{q}_2 \underset{\sim}{q}_3 \underset{\sim}{q}_4 \\ j_1 j_2 j_3 j_4}} f^4(\underset{\sim}{q}_1 j_1, \underset{\sim}{q}_2 j_2, \underset{\sim}{q}_3 j_3, \underset{\sim}{q}_4 j_4)$$

$$\times\, \Delta(\underset{\sim}{q}+\underset{\sim}{q}_2+\underset{\sim}{q}_3+\underset{\sim}{q}_4)\, \Delta(-\underset{\sim}{q}+\underset{\sim}{q}_1)\, J_4^B \tag{2.16}$$

$$S_4^C(\underset{\sim}{q},\omega) = \left(\frac{1}{2!}\right)^2 \sum_{\substack{\underset{\sim}{q}_1 \underset{\sim}{q}_2 \underset{\sim}{q}_3 \underset{\sim}{q}_4 \\ j_1 j_2 j_3 j_4}} f^4(\underset{\sim}{q}_1 j_1, \underset{\sim}{q}_2 j_2, \underset{\sim}{q}_3 j_3, \underset{\sim}{q}_4 j_4)$$

$$\times\, \Delta(-\underset{\sim}{q}+\underset{\sim}{q}_1+\underset{\sim}{q}_2)\, \Delta(\underset{\sim}{q}+\underset{\sim}{q}_3+\underset{\sim}{q}_4)\, J_4^C \tag{2.17}$$

and in particular

$$f^3(\underset{\sim}{q}_1 j_1, \underset{\sim}{q}_2 j_2, \underset{\sim}{q}_3 j_3)$$

$$= \frac{iN}{2!}\left(\frac{\hbar}{2NM}\right)^{3/2} \frac{(\underset{\sim}{q}\cdot \underset{\sim}{\varepsilon}_{\underset{\sim}{q}_1 j_1})(\underset{\sim}{q}\cdot \underset{\sim}{\varepsilon}_{\underset{\sim}{q}_2 j_2})(\underset{\sim}{q}\cdot \underset{\sim}{\varepsilon}_{\underset{\sim}{q}_3 j_3})}{(\omega_{\underset{\sim}{q}_1 j_1}\,\omega_{\underset{\sim}{q}_2 j_2}\,\omega_{\underset{\sim}{q}_3 j_3})^{1/2}} \tag{2.18}$$

$$f^4(\underset{\sim}{q}_1 j_1, \underset{\sim}{q}_2 j_2, \underset{\sim}{q}_3 j_3, \underset{\sim}{q}_4 j_4)$$

$$= N\left(\frac{\hbar}{2NM}\right)^2 \frac{(\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}_1 j_1})(\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}_2 j_2})(\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}_3 j_3})(\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}_4 j_4})}{(\omega_{\underset{\sim}{q}_1 j_1}\,\omega_{\underset{\sim}{q}_2 j_2}\,\omega_{\underset{\sim}{q}_3 j_3}\,\omega_{\underset{\sim}{q}_4 j_4})^{1/2}} \tag{2.19}$$

$$J_2 = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\; e^{i\omega t}\left\langle A_{\underset{\sim}{q}_1 j_1}(t)\, A_{\underset{\sim}{q}_2 j_2}(0)\right\rangle \tag{2.20}$$

$$J_3^A = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\; e^{i\omega t}\left\langle A_{\underset{\sim}{q}_1 j_1}(t)\, A_{\underset{\sim}{q}_2 j_2}(t)\, A_{\underset{\sim}{q}_3 j_3}(0)\right\rangle \tag{2.21}$$

$$J_3^B = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\; e^{i\omega t}\left\langle A_{\underset{\sim}{q}_1 j_1}(t)\, A_{\underset{\sim}{q}_2 j_2}(0)\, A_{\underset{\sim}{q}_3 j_3}(0)\right\rangle \tag{2.22}$$

$$J_4^A = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\; e^{i\omega t}\left\langle A_{\underset{\sim}{q}_1 j_1}(t)\, A_{\underset{\sim}{q}_2 j_2}(t)\, A_{\underset{\sim}{q}_3 j_3}(t)\, A_{\underset{\sim}{q}_4 j_4}(0)\right\rangle \tag{2.23}$$

$$J_4^B = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\; e^{i\omega t}\left\langle A_{\underset{\sim}{q}_1 j_1}(t)\, A_{\underset{\sim}{q}_2 j_2}(0)\, A_{\underset{\sim}{q}_3 j_3}(0)\, A_{\underset{\sim}{q}_4 j_4}(0)\right\rangle \tag{2.24}$$

$$J_4^C = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\; e^{i\omega t}\left\langle A_{\underset{\sim}{q}_1 j_1}(t)\, A_{\underset{\sim}{q}_2 j_2}(t)\, A_{\underset{\sim}{q}_3 j_3}(0)\, A_{\underset{\sim}{q}_4 j_4}(0)\right\rangle \tag{2.25}$$

The integrands arising in Eqs. (2.20) to (2.25) can be evaluated by two different methods:

a) the Green function approach (see Shukla and Muller (1971))

b) the straight forward approach of the calculation of the matrix elements (matrix element method).

Without indulging in excessive tedious algebra, it is possible to derive the contributions to ρ from the harmonic, QS, DW and MP processes by the matrix element method, whereas the remaining contributions (CS, W and I) are extremely tedious to evaluate by this method.

In the next few sections, we present a derivation of harmonic, QS, DW and MP contributions to ρ and a summary of the remaining contributions (CS, W and I) obtained by the Green function method (Shukla and Muller (1979)).

2.1 DERIVATION OF $S_2(\underset{\sim}{q},\omega)$

We shall now concentrate on the derivation of the thermal average $\langle A\underset{\sim}{q}_1 j_1(t) A\underset{\sim}{q}_2 j_2(0)\rangle$ arising in Eq. (2.20). Replacing the operator 0 in Eq. (2.4) by $A\underset{\sim}{q}_1 j_1(t) A\underset{\sim}{q}_2 j_2(0)$ and substituting for the Hamiltonian H (Eq. (2.5)) we obtain the following

$$\langle A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0)\rangle = \frac{Tr\, e^{-\beta(H_0+H_A)} A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0)}{Tr\, e^{-\beta(H_0+H_A)}} \qquad (2.26)$$

In order to evaluate Eq. (2.25), we first expand the exponential $e^{-\beta(H_0+H_A)}$ carefully in powers of H_A. Using the procedure outlined by Goldberger and E. N. Adams II (1952) we have

$$e^{-\beta(H_0+H_A)} = e^{-\beta H_0}\Big[1 - \int_0^\beta H_A(\beta')\,d\beta' + \int_0^\beta\int_0^{\beta'} H_A(\beta')\,H_A(\beta'')\,d\beta'\,d\beta'' - \cdots\Big] \qquad (2.27)$$

where $\quad H_A(\beta) = e^{\beta H_0} H_A e^{-\beta H_0}$

Substituting the expansion Eq. (2.27) into Eq. (2.26) and approximating the denominator by $Tr e^{-\beta H_0}$ (i.e. disregarding anharmonic effects), we obtain

$$\langle A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0)\rangle = \frac{Tr\, e^{-\beta H_0} A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0)}{Tr\, e^{-\beta H_0}}$$

$$- \frac{Tr\, e^{-\beta H_0}\int_0^\beta H_A(\beta')\, A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0)\, d\beta'}{Tr\, e^{-\beta H_0}}$$

$$+ \frac{Tr\, e^{-\beta H_0}\int_0^\beta\int_0^{\beta'} H_A(\beta')\, H_A(\beta'')\, A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0)\, d\beta'\, d\beta''}{Tr\, e^{-\beta H_0}}$$

$$- \cdots$$

$$= \langle A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0) \rangle_0 + \langle A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0) \rangle_1$$

$$+ \langle A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0) \rangle_2 + \cdots \tag{2.28}$$

Substituting Eq. (2.28) into the expression for J_2 (Eq. (2.20)) and then substituting J_2 into Eq. (2.12) we can write $S_2(\underset{\sim}{q}, \omega)$ as follows:

$$S_2(\underset{\sim}{q}, \omega) = \left[S_2(\underset{\sim}{q}, \omega)\right]_0 + \left[S_2(\underset{\sim}{q}, \omega)\right]_1 + \left[S_2(\underset{\sim}{q}, \omega)\right]_2 \tag{2.28a}$$

The first term arising in Eq. (2.28) is the Harmonic part of the thermal average $\langle A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0) \rangle$.

The only nonvanishing contribution in the detailed calculation of the average of the type $\langle A_{\underset{\sim}{q}_1 j_1}(t)\ A_{\underset{\sim}{q}_2 j_2}(0) \rangle_0$ comes from the condition $\delta_{\underset{\sim}{q}_1, -\underset{\sim}{q}_2}\ \delta_{j_1, j_2}$. This allows the annihilation and creation operators to act on the same state. Hence we incorporate this condition in evaluating the average of the matrix element $A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0)$. Explicitly the average is given by

$$\langle A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0) \rangle_0 = \frac{\mathrm{Tr}\, e^{-\beta H_0} A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0)\ \delta_{\underset{\sim}{q}_1, -\underset{\sim}{q}_2} \delta_{j_1, j_2}}{\mathrm{Tr}\, e^{-\beta H_0}}$$

$$= \frac{\sum_n \langle n | e^{-\beta H_0} A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0) | n \rangle \quad \delta_{\underset{\sim}{q}_1, -\underset{\sim}{q}_2} \delta_{j_1, j_2}}{\sum_n \langle n | e^{-\beta H_0} | n \rangle}$$

$$= \frac{\sum_n e^{-\beta E_n} \langle n | A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0) | n \rangle \quad \delta_{\underset{\sim}{q}_1, -\underset{\sim}{q}_2} \delta_{j_1, j_2}}{\sum_n e^{-\beta E_n}} \tag{2.29}$$

where in Eq. (2.29) the phonon state $|n\rangle$ is completely represented by

$$|n\rangle \equiv |n_{q_1j_1}\rangle |n_{q_2j_2}\rangle \cdots |n_{q_Nj_N}\rangle$$

$$= |n_{q_1j_1}, n_{q_2j_2}, \cdots n_{q_Nj_N}\rangle$$

and $n_{q_ij_i}$ (i = 1,2,...N) represents the occupancy number of the state (i). In obtaining the second line in Eq. (2.29), we have made use of the eigenvalue equation,

$$H_o|n\rangle = \hbar\omega_n(n+\tfrac{1}{2}) = E_n|n\rangle$$

and

$$\langle n|e^{-\beta H_o} = \langle n|e^{-\beta E_n} \qquad (2.30)$$

The phonon operators a_{qj} and a^+_{qj} obey the following operational definition,

$$a^+_{qj}|n\rangle = \sqrt{n_{qj}+1}\,|n_{qj}+1, n_{q_2j_2}, n_{q_3j_3}, \cdots n_{q_Nj_N}\rangle \qquad (2.31a)$$

$$a_{qj}|n\rangle = \sqrt{n_{qj}}\,|n_{qj}-1, n_{q_2j_2}, n_{q_3j_3}, \cdots n_{q_Nj_N}\rangle \qquad (2.31b)$$

Substituting for the operators $A_{q_1j_1}(t)$ and $A_{q_2j_2}(0)$, Eq. (2.29) can be rewritten in the following form:

$$\langle A_{q_1j_1}(t)\,A_{q_2j_2}(0)\rangle_0 = \sum_n e^{-\beta E_n}\langle n|e^{iH_ot/\hbar}(a^+_{-q_1j_1} + a_{q_1j_1})$$

$$\times\, e^{-iH_ot/\hbar}(a^+_{-q_2j_2} + a_{q_2j_2})|n\rangle \Big/ \sum_n e^{-\beta E_n}$$

$$= \sum_n e^{-\beta E_n} e^{iE_nt/\hbar}\Big[\langle n|a^+_{-q_1j_1}\, e^{-iH_ot/\hbar}\, a^+_{-q_2j_2}|n\rangle$$

$$+ \langle n | a^{+}_{-\underset{\sim}{q}_1 j_1} e^{-iH_0 t/\hbar} a_{\underset{\sim}{q}_2 j_2} | n \rangle$$

$$+ \langle n | a_{\underset{\sim}{q}_1 j_1} e^{-iH_0 t/\hbar} a^{+}_{-\underset{\sim}{q}_2 j_2} | n \rangle$$

$$+ \langle n | a_{\underset{\sim}{q}_1 j_1} e^{-iH_0 t/\hbar} a_{\underset{\sim}{q}_2 j_2} | n \rangle \Big] \Big/ \sum_n e^{-\beta E_n} \qquad (2.32)$$

First letting the operators ($a_{\underset{\sim}{q}_1 j_1}$ or $a^{+}_{\underset{\sim}{q}_2 j_2}$) act on the state $|n\rangle$ in Eq. (2.32) and then acting on the resulting state with the operator $e^{-iH_0 t/\hbar}$, we obtain the following:

$$\langle A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0) \rangle_0 = \sum_n e^{-\beta E_n} e^{iE_n t/\hbar}$$

$$\times \Big[e^{-i(E_{n_{\underset{\sim}{q}_1 j_1}+1})t/\hbar} \sqrt{n_{\underset{\sim}{q}_1 j_1}+1} \sqrt{n_{\underset{\sim}{q}_1 j_1}+2} \langle n | n_{\underset{\sim}{q}_1 j_1}+2 \rangle$$

$$+ e^{-i(E_{n_{\underset{\sim}{q}_1 j_1}-1})t/\hbar} n_{\underset{\sim}{q}_1 j_1} \langle n | n \rangle + e^{-i(E_{n_{\underset{\sim}{q}_1 j_1}+1})} (n_{\underset{\sim}{q}_1 j_1}+1) \langle n | n \rangle$$

$$+ e^{-i(E_{n_{\underset{\sim}{q}_1 j_1}-1})t/\hbar} \sqrt{n_{\underset{\sim}{q}_1 j_1}} \sqrt{n_{\underset{\sim}{q}_1 j_1}-1} \langle n | n_{\underset{\sim}{q}_1 j_1}-2 \rangle \Big]$$

$$\times \delta_{\underset{\sim}{q}_1, -\underset{\sim}{q}_2} \delta_{j_1, j_2} \Big/ \sum_n e^{-\beta E_n} \qquad (2.33)$$

Using the orthonormality condition of the states the first and last terms arising in the R.H.S. of Eq. (2.33) are zero.

Performing the sum over n in Eq. (2.33) which amounts to replacing $n_{\underset{\sim}{q}j}$ by its average $\bar{n}_{\underset{\sim}{q}j} = \dfrac{1}{e^{\beta\hbar\omega_{\underset{\sim}{q}j}}-1}$, we obtain

$$\langle A_{\underset{\sim}{q}_1 j_1}(t)\, A_{\underset{\sim}{q}_2 j_2}(0)\rangle_0 = \left[e^{i\omega_{\underset{\sim}{q}_1 j_1} t}\,\bar{n}_{\underset{\sim}{q}_1 j_1} + e^{-i\omega_{\underset{\sim}{q}_1 j_1} t}(\bar{n}_{\underset{\sim}{q}_1 j_1}+1)\right] \times \delta_{\underset{\sim}{q}_1,\underset{\sim}{q}_2}\,\delta_{j_1 j_2} \tag{2.34}$$

Substituting Eq. (2.34) into Eq. (2.20) and performing the trivial integration over the time coordinate which yields a delta function, we obtain the following expression for J_2:

$$J_2 = \left[(\bar{n}_{\underset{\sim}{q}_1 j_1}+1)\,\delta(\omega - \omega_{\underset{\sim}{q}_1 j_1}) + \bar{n}_{\underset{\sim}{q}_1 j_1}\,\delta(\omega + \omega_{\underset{\sim}{q}_1 j_1})\right]\delta_{\underset{\sim}{q}_1,\underset{\sim}{q}_2}\,\delta_{j_1 j_2} \tag{2.35}$$

Substituting this result for J_2 into Eq. (2.12), we obtain finally the following expression for $[S_2(\underset{\sim}{q},\omega)]_0$, viz.,

$$[S_2(\underset{\sim}{q},\omega)]_0 = \left(\frac{\hbar}{2M}\right)\sum_j \frac{|\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}|^2}{\omega_{\underset{\sim}{q}j}}\Big[(n_{\underset{\sim}{q}j}+1)\,\delta(\omega-\omega_{\underset{\sim}{q}j}) + n_{\underset{\sim}{q}j}\,\delta(\omega+\omega_{\underset{\sim}{q}j})\Big] \tag{2.36}$$

where the $[S_2(q,\omega)]_0$ indicates the harmonic contribution to $S_2(q,\omega)$.

The contribution to the second term arising in Eq. (2.28) comes from the quartic term of H_A (Eq. (2.5)] only as the cubic term contributes nothing (odd number of operators). $H_A(\beta')$ is given by

$$H_A(\beta') = \sum_{\substack{\underset{\sim}{q}_3\underset{\sim}{q}_4\underset{\sim}{q}_5\underset{\sim}{q}_6\\ j_3 j_4 j_5 j_6}} V^4(\underset{\sim}{q}_3 j_3, \underset{\sim}{q}_4 j_4, \underset{\sim}{q}_5 j_5, \underset{\sim}{q}_6 j_6) \times A_{\underset{\sim}{q}_3 j_3}(\beta')\, A_{\underset{\sim}{q}_4 j_4}(\beta')\, A_{\underset{\sim}{q}_5 j_5}(\beta')\, A_{\underset{\sim}{q}_6 j_6}(\beta') \tag{2.37}$$

where $$A_{\underset{\sim}{q}j}(\beta') = e^{\beta H_0} A_{\underset{\sim}{q}j}(0)\, e^{-\beta H_0} \tag{2.38}$$

Using the same procedure as in the derivation of $\left\langle A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0)\right\rangle_0$ we can write $\left\langle A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0)\right\rangle_1$ as

$$\left\langle A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0)\right\rangle_1 = - \frac{\sum_n e^{-\beta E_n} \int_0^\beta \langle n | H_A(\beta') A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0) | n \rangle \, d\beta'}{\sum_n e^{-\beta E_n}} \tag{2.39}$$

Substituting for $H_A(\beta')$ from Eq. (2.37) into Eq. (2.39) and employing Eq. (2.38), we obtain the following

$$\left\langle A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0)\right\rangle_1 = -\sum_n e^{-\beta E_n} \sum_{\substack{\underset{\sim}{q}_3 \underset{\sim}{q}_4 \underset{\sim}{q}_5 \underset{\sim}{q}_6 \\ j_3 j_4 j_5 j_6}} V^4(\underset{\sim}{q}_3 j_3, \underset{\sim}{q}_4 j_4, \underset{\sim}{q}_5 j_5, \underset{\sim}{q}_6 j_6)$$

$$\times \int_0^\beta \langle n | e^{\beta' H_0} A_{\underset{\sim}{q}_3 j_3}(0) A_{\underset{\sim}{q}_4 j_4}(0) A_{\underset{\sim}{q}_5 j_5}(0) A_{\underset{\sim}{q}_6 j_6}(0) e^{-\beta' H_0} e^{i H_0 t/\hbar}$$

$$\times A_{\underset{\sim}{q}_1 j_1}(0) e^{-i H_0 t/\hbar} A_{\underset{\sim}{q}_2 j_2}(0) | n \rangle \, d\beta' \Big/ \sum_n e^{-\beta E_n} \tag{2.40}$$

The only nonvanishing contribution in the detailed calculation of the averages $\left\langle A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(0)\right\rangle_1$ will come from the conditions $\delta_{\underset{\sim}{q}_1 - \underset{\sim}{q}_2}$, $\delta_{\underset{\sim}{q}_3 - \underset{\sim}{q}_4}$, $\delta_{\underset{\sim}{q}_5 - \underset{\sim}{q}_6}$, $\delta_{\underset{\sim}{q}_1 \underset{\sim}{q}_3}$, $\delta_{j_1 j_2}$, $\delta_{j_5 j_6}$, $\delta_{j_3 j_4}$ and $\delta_{j_1 j_3}$. These conditions ensure that an equal number of creation annihilation operators act on the same state . Since the decision of which operator is coupled to which is arbitrary and since we can have twelve different ways of coupling the operators, we introduce a factor of 12. Substituting for the operators $A_{\underset{\sim}{q} j}$ in terms of the phonon creation ($a^+_{\underset{\sim}{q} j}$) and annihilation ($a_{\underset{\sim}{q} j}$) operators, Eq (2.40) can be written as:

$$\langle A_{\underset{\sim}{q}_1 j_1}(t)\, A_{\underset{\sim}{q}_2 j_2}(0)\rangle_1 = -12 \sum_n e^{-\beta E_n} \sum_{\substack{q_3 q_4 q_5 q_6 \\ j_3 j_4 j_5 j_6}} V^4(\underset{\sim}{q}_3 j_3, \underset{\sim}{q}_4 j_4, \underset{\sim}{q}_5 j_5, \underset{\sim}{q}_6 j_6)$$

$$\times \int_0^\beta \langle n| e^{\beta H_0} (a^+_{-\underset{\sim}{q}_3 j_3} + a_{\underset{\sim}{q}_3 j_3})(a^+_{-\underset{\sim}{q}_4 j_4} + a_{\underset{\sim}{q}_4 j_4})(a^+_{-\underset{\sim}{q}_5 j_5} + a_{\underset{\sim}{q}_5 j_5})$$

$$\times (a^+_{-\underset{\sim}{q}_6 j_6} + a_{\underset{\sim}{q}_6 j_6})\, e^{-\beta H_0}\, e^{i H_0 t/\hbar}\, (a^+_{-\underset{\sim}{q}_1 j_1} + a_{\underset{\sim}{q}_1 j_1})\, e^{-i H_0 t/\hbar}$$

$$\times (a^+_{-\underset{\sim}{q}_2 j_2} + a_{\underset{\sim}{q}_2 j_2})\, |n\rangle\, d\beta'\, \delta_{\underset{\sim}{q}_1 - \underset{\sim}{q}_2}\, \delta_{\underset{\sim}{q}_3 - \underset{\sim}{q}_4}\, \delta_{\underset{\sim}{q}_5 - \underset{\sim}{q}_6}$$

$$\times \delta_{\underset{\sim}{q}_1 \underset{\sim}{q}_3}\, \delta_{j_1 j_2}\, \delta_{j_3 j_4}\, \delta_{j_5 j_6}\, \delta_{j_1 j_3} \qquad (2.41)$$

Upon expanding the matrix element in Eq. (2.41), we find that there are only eight terms which have an equal number of creation and annihilation operators and they are the only ones which will give a non-zero contribution.

Letting the operators $a^+_{-\underset{\sim}{q}j}$ and $a_{\underset{\sim}{q}j}$ act on the state $|n\rangle$, using the eigenvalue equation (2.30) and the normalization condition $\langle n/n\rangle = 1$ we obtain the following expression for the correlation function.

$$\langle A_{\underset{\sim}{q}_1 j_1}(t)\, A_{\underset{\sim}{q}_2 j_2}(0)\rangle_1 = -12 \sum_n e^{-\beta E_n} \sum_{\underset{\sim}{q}_5 j_5} V^4(\underset{\sim}{q}_1 j_1, -\underset{\sim}{q}_1 j_1, \underset{\sim}{q}_5 j_5, -\underset{\sim}{q}_5 j_5)$$

$$\times \left[(n_{\underset{\sim}{q}_1 j_1} + 1)\, e^{-i\omega_{\underset{\sim}{q}_1 j_1} t} + n_{\underset{\sim}{q}_1 j_1}\, e^{i\omega_{\underset{\sim}{q}_1 j_1} t} \right]$$

$$\times \left[n_{\underset{\sim}{q}_1 j_1} n_{\underset{\sim}{q}_5 j_5} + n_{\underset{\sim}{q}_1 j_1}(n_{\underset{\sim}{q}_5 j_5} + 1) + (n_{\underset{\sim}{q}_1 j_1} + 1) n_{\underset{\sim}{q}_5 j_5} + (n_{\underset{\sim}{q}_1 j_1} + 1)(n_{\underset{\sim}{q}_5 j_5} + 1) \right]$$

$$\times \int_0^\beta d\beta' \Big/ \sum_n e^{-\beta E_n} \qquad (2.42)$$

Performing the trivial integration over β' and the sum over n in Eq. (2.42), which amounts to replacing $n_{\underset{\sim}{q}j}$ by $\bar{n}_{\underset{\sim}{q}j}$, we obtain

$$\left\langle A_{\underset{\sim}{q}_1 j_1}(t)\, A_{\underset{\sim}{q}_2 j_2}(0)\right\rangle_1 = -12 \sum_{\underset{\sim}{q}_5 j_5} V^4(\underset{\sim}{q}_1 j_1, -\underset{\sim}{q}_1 j_1, \underset{\sim}{q}_5 j_5, -\underset{\sim}{q}_5 j_5)\,\beta$$

$$\times \left[(\bar{n}_{\underset{\sim}{q}_1 j_1}+1)\, e^{-i\omega_{\underset{\sim}{q}_1 j_1} t} + \bar{n}_{\underset{\sim}{q}_1 j_1}\, e^{i\omega_{\underset{\sim}{q}_1 j_1} t}\right]$$

$$\times \left[\bar{n}_{\underset{\sim}{q}_1 j_1}\bar{n}_{\underset{\sim}{q}_5 j_5} + \bar{n}_{\underset{\sim}{q}_1 j_1}(\bar{n}_{\underset{\sim}{q}_5 j_5}+1) + (\bar{n}_{\underset{\sim}{q}_1 j_1}+1)\bar{n}_{\underset{\sim}{q}_5 j_5} + (\bar{n}_{\underset{\sim}{q}_1 j_1}+1)(\bar{n}_{\underset{\sim}{q}_5 j_5}+1)\right] \tag{2.43}$$

Substituting Eq. (2.43) into the expression for J_2 (Eq. (2.20)) and performing the trivial integration over time coordinate, we have the following expression for the contribution to J_2 from the quartic term of the Hamiltonian $([J_2]_q)$

$$[J_2]_q = -12 \sum_{\underset{\sim}{q}_5 j_5} V^4(\underset{\sim}{q}_1 j_1, -\underset{\sim}{q}_1 j_1, \underset{\sim}{q}_5 j_5, -\underset{\sim}{q}_5 j_5)$$

$$\times \left[(\bar{n}_{\underset{\sim}{q}_1 j_1}+1)\,\delta(\omega - \omega_{\underset{\sim}{q}_1 j_1}) + \bar{n}_{\underset{\sim}{q}_1 j_1}\,\delta(\omega + \omega_{\underset{\sim}{q}_1 j_1})\right]$$

$$\times \left[\bar{n}_{\underset{\sim}{q}_1 j_1}\bar{n}_{\underset{\sim}{q}_5 j_5} + \bar{n}_{\underset{\sim}{q}_1 j_1}(\bar{n}_{\underset{\sim}{q}_5 j_5}+1) + (\bar{n}_{\underset{\sim}{q}_1 j_1}+1)\bar{n}_{\underset{\sim}{q}_5 j_5} + (\bar{n}_{\underset{\sim}{q}_1 j_1}+1)(\bar{n}_{\underset{\sim}{q}_5 j_5}+1)\right] \tag{2.44}$$

Substituting this result for $[J_2]_q$ into Eq. (2.12) we obtain finally the following expression for $[S_2(\underset{\sim}{q},\omega)]_1$, viz.,

$$\left[S_2(\underset{\sim}{q},\omega) \right]_1 = -12\left(\frac{\hbar}{2M}\right)\beta \sum_{\underset{\sim}{q}_1 j_1} \frac{(\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j})(\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j})}{\omega_{\underset{\sim}{q}j}^{\;2}} V^4(\underset{\sim}{q}j,-\underset{\sim}{q}j,\underset{\sim}{q}_1 j_1,-\underset{\sim}{q}_1 j_1)$$

$$\times \left[\bar{n}_{\underset{\sim}{q}j}\,\delta(\omega+\omega_{\underset{\sim}{q}j}) + (\bar{n}_{\underset{\sim}{q}j}+1)\,\delta(\omega-\omega_{\underset{\sim}{q}j}) \right]$$

$$\times \left[\bar{n}_{\underset{\sim}{q}_1 j_1}\bar{n}_{\underset{\sim}{q}j} + (\bar{n}_{\underset{\sim}{q}_1 j_1}+1)\,\bar{n}_{\underset{\sim}{q}j} + \bar{n}_{\underset{\sim}{q}_1 j_1}(\bar{n}_{\underset{\sim}{q}j}+1) \right.$$

$$\left. + (\bar{n}_{\underset{\sim}{q}_1 j_1}+1)(\bar{n}_{\underset{\sim}{q}j}+1) \right] \qquad (2.45)$$

where in Eq. (2.45) we have replaced the dummy index $\underset{\sim}{q}_5 j_5$ by $\underset{\sim}{q}_1 j_1$.

The third term arising in Eq. (2.28) can be derived in the same manner, but this is very lengthy. The contribution to ρ from this term and another contribution to ρ arising from the three displacement operators and the $V^3(\underset{\sim}{q}_1 j_1,\underset{\sim}{q}_2 j_2,\underset{\sim}{q}_3 j_3)$ term in H has been obtained by Shukla and Muller (1979) using a Green function approach. These results are presented in Section 3.

2.2. DERIVATION OF $S_4(\underset{\sim}{q},\omega)$ IN THE HARMONIC APPROXIMATION

We shall now concentrate on the derivation of J_4^A. Applying Wick's theorem to decouple the correlation functions (which is exact in this case as can be seen by detailed derivation) in Eq. (2.23), we obtain the following form for J_4^A:

$$J_4^A = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{i\omega t}\Big[\langle A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(t)\rangle\langle A_{\underset{\sim}{q}_3 j_3}(t) A_{\underset{\sim}{q}_4 j_4}(0)\rangle$$

$$+ \langle A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_3 j_3}(t)\rangle\langle A_{\underset{\sim}{q}_2 j_2}(t) A_{\underset{\sim}{q}_4 j_4}(0)\rangle$$

$$+ \langle A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_4 j_4}(0)\rangle\langle A_{\underset{\sim}{q}_2 j_2}(t) A_{\underset{\sim}{q}_3 j_3}(t)\rangle\Big]\, dt \qquad (2.46)$$

The equal time correlation function $\langle A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(t)\rangle$ can be evaluated in the same manner as described in Sec. 2.1 giving us

$$\langle A_{\underset{\sim}{q}j}(t) A_{\underset{\sim}{q}'j'}(t)\rangle = \left[(\bar{n}_{\underset{\sim}{q}j}+1) + \bar{n}_{\underset{\sim}{q}j}\right]\delta_{\underset{\sim}{q},-\underset{\sim}{q}'}\,\delta_{jj'} \qquad (2.47)$$

and from Sec. 2.1 we also have,

$$\langle A_{\underset{\sim}{q}j}(t) A_{\underset{\sim}{q}'j'}(0)\rangle = \left[(\bar{n}_{\underset{\sim}{q}j}+1)\, e^{-i\omega_{\underset{\sim}{q}j}t} + \bar{n}_{\underset{\sim}{q}j}\, e^{i\omega_{\underset{\sim}{q}j}t}\right]$$

$$\times\ \delta_{\underset{\sim}{q}-\underset{\sim}{q}'}\,\delta_{jj'} \qquad (2.48)$$

When Eq. (2.46) is substituted into Eq. (2.15) the three terms are found to be equivalent on relabelling of the vectors $\underset{\sim}{q}$ and the branch indices j. Making use of this equality and substituting for the correlation functions from Eqs. (2.47) and (2.48), we find for the integral J_4^A

$$J_4^A = \frac{3}{2\pi}\int_{-\infty}^{+\infty} e^{i\omega t}\left[(\bar{n}_{\underset{\sim}{q}_1 j_1}+1)+\bar{n}_{\underset{\sim}{q}_1 j_1}\right]$$

$$\times\left[(\bar{n}_{\underset{\sim}{q}_3 j_3}+1)\, e^{-i\omega_{\underset{\sim}{q}_3 j_3} t}+\bar{n}_{\underset{\sim}{q}_3 j_3}\, e^{i\omega_{\underset{\sim}{q}_3 j_3} t}\right]$$

$$\times\, \delta_{\underset{\sim}{q}_1-\underset{\sim}{q}_2}\,\delta_{\underset{\sim}{q}_3-\underset{\sim}{q}_4}\,\delta_{j_1 j_2}\,\delta_{j_3 j_4}\, dt$$

Performing the trivial integration over the time coordinate, the final form for J_4^A is given by:

$$J_4^A = 3\left[(\bar{n}_{\underset{\sim}{q}_1 j_1}+1)+\bar{n}_{\underset{\sim}{q}_1 j_1}\right]\left[(\bar{n}_{\underset{\sim}{q}_3 j_3}+1)\,\delta(\omega-\omega_{\underset{\sim}{q}_3 j_3})\right.$$

$$\left.+\,\bar{n}_{\underset{\sim}{q}_3 j_3}\,\delta(\omega+\omega_{\underset{\sim}{q}_3 j_3})\right]\delta_{\underset{\sim}{q}_1-\underset{\sim}{q}_2}\,\delta_{\underset{\sim}{q}_3-\underset{\sim}{q}_4}\,\delta_{j_1 j_2}\,\delta_{j_3 j_4} \tag{2.49}$$

Substituting Eq. (2.49) into Eq. (2.15) the four sums over the wave vector $\underset{\sim}{q}$ and another four sums over the branch index j reduce to a single sum over $\underset{\sim}{q}$ and a double sum over j and j_1. The final expression for $S_4^A(\underset{\sim}{q},\omega)$ can be rearranged in the following form, viz.,

$$S_4^A(\underset{\sim}{q},\omega) = -\frac{N}{3!}\left(\frac{\hbar}{2NM}\right)^2 3\sum_j \frac{|\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}|^2}{\omega_{\underset{\sim}{q}j}}$$

$$\times\left[(\bar{n}_{\underset{\sim}{q}j}+1)\,\delta(\omega-\omega_{\underset{\sim}{q}j})+\bar{n}_{\underset{\sim}{q}j}\,\delta(\omega+\omega_{\underset{\sim}{q}j})\right]$$

$$\times\sum_{\underset{\sim}{q}_1 j_1}\frac{|\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}_1 j_1}|^2}{\omega_{\underset{\sim}{q}_1 j_1}}\left[(\bar{n}_{\underset{\sim}{q}_1 j_1}+1)+\bar{n}_{\underset{\sim}{q}_1 j_1}\right] \tag{2.50}$$

Similarly for the evaluation of J_4^B, we apply the Wick's theorem to the integrand in Eq. (2.24) and obtain the following:

$$J_4^B = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{i\omega t}\Big[\langle A_{\underset{\sim}{q}_1 j_1}(t)A_{\underset{\sim}{q}_2 j_2}(0)\rangle\langle A_{\underset{\sim}{q}_3 j_3}(0)A_{\underset{\sim}{q}_4 j_4}(0)\rangle$$

$$+\langle A_{\underset{\sim}{q}_1 j_1}(t)A_{\underset{\sim}{q}_3 j_3}(0)\rangle\langle A_{\underset{\sim}{q}_2 j_2}(0)A_{\underset{\sim}{q}_4 j_4}(0)\rangle$$

$$+\langle A_{\underset{\sim}{q}_1 j_1}(t)A_{\underset{\sim}{q}_4 j_4}(0)\rangle\langle A_{\underset{\sim}{q}_2 j_2}(0)A_{\underset{\sim}{q}_3 j_3}(0)\rangle\Big]dt \qquad (2.51)$$

In the expression for J_4^B (Eq. (2.51)) we again have the product of an equal time correlation function and an unequal time correlation function. The difference being that the equal time correlation function is now to be evaluated at t = 0, instead of t ≠ 0 as in J_4^A (Eq. 2.46). Since $\langle A_{\underset{\sim}{q}_1 j_1}(0)A_{\underset{\sim}{q}_2 j_2}(0)\rangle = \langle A_{\underset{\sim}{q}_1 j_1}(t)A_{\underset{\sim}{q}_2 j_2}(t)\rangle$ it is clear that $J_4^A = J_4^B$ which means $S_4^A(\underset{\sim}{q},\omega) = S_4^B(\underset{\sim}{q},\omega)$. Thus we can write:

$$S_4^{A+B}(\underset{\sim}{q},\omega) = S_4^A(\underset{\sim}{q},\omega) + S_4^B(\underset{\sim}{q},\omega) = 2S_4^A(\underset{\sim}{q},\omega)$$

$$= -\frac{6N}{3!}\left(\frac{\hbar}{2NM}\right)^2 \sum_j \frac{|\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}|^2}{\omega_{\underset{\sim}{q}j}}\Big[(\bar{n}_{\underset{\sim}{q}j}+1)\delta(\omega-\omega_{\underset{\sim}{q}j})$$

$$+\bar{n}_{\underset{\sim}{q}j}\,\delta(\omega+\omega_{\underset{\sim}{q}j})\Big]\sum_{\underset{\sim}{q}_1 j_1}\frac{|\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}_1 j_1}|^2}{\omega_{\underset{\sim}{q}_1 j_1}}$$

$$\times\Big[(n_{\underset{\sim}{q}_1 j_1}+1)+n_{\underset{\sim}{q}_1 j_1}\Big] \qquad (2.52)$$

Finally, when Wick's theorem is applied in evaluating the average of the operators arising in the integrand of J_4^C as given by Eq. (2.25), we obtain.

$$J_4^c = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{i\omega t}\Big[\langle A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_2 j_2}(t)\rangle\langle A_{\underset{\sim}{q}_3 j_3}(0) A_{\underset{\sim}{q}_4 j_4}(0)\rangle$$

$$+ \langle A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_3 j_3}(0)\rangle\langle A_{\underset{\sim}{q}_2 j_2}(t) A_{\underset{\sim}{q}_4 j_4}(0)\rangle$$

$$+ \langle A_{\underset{\sim}{q}_1 j_1}(t) A_{\underset{\sim}{q}_4 j_4}(0)\rangle\langle A_{\underset{\sim}{q}_2 j_2}(t) A_{\underset{\sim}{q}_3 j_3}(0)\rangle\Big] dt$$

$$= J_4^c(1) + J_4^c(2) + J_4^c(3) \tag{2.53}$$

The first term in Eq. (2.53) contains the product of two equal time correlation functions, and when this term is evaluated, we obtain the following:

$$J_4^c(1) = (2\bar{n}_{\underset{\sim}{q}_1 j_1}+1)(2\bar{n}_{\underset{\sim}{q}_3 j_3}+1)\,\delta_{\underset{\sim}{q}_1 - \underset{\sim}{q}_2}\,\delta_{\underset{\sim}{q}_3 - \underset{\sim}{q}_4}\,\delta_{j_1 j_2}\,\delta_{j_3 j_4}$$

$$\times \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{i\omega t}\, dt$$

$$= (2\bar{n}_{\underset{\sim}{q}_1 j_1}+1)(2\bar{n}_{\underset{\sim}{q}_3 j_3}+1)\,\delta_{\underset{\sim}{q}_1 - \underset{\sim}{q}_2}\,\delta_{\underset{\sim}{q}_3 - \underset{\sim}{q}_4}\,\delta_{j_1 j_2}\,\delta_{j_3 j_4}\,\delta(\omega)$$

This means that the only contribution to ρ would be arising from $\omega = 0$ which represents the elastic scattering and hence does not contribute to ρ .

Using the same procedure as in the evaluation of J_4^A and noting that when Eq. (2.53) is substituted into Eq. (2.17) the last two terms of Eq. (2.53) are found to be equivalent. Thus we can write J_4^C as follows:

$$J_4^c = \frac{2}{2\pi}\int_{-\infty}^{+\infty} e^{i\omega t}\left[(\bar{n}_{\mathbf{q}_1 j_1}+1)e^{-i\omega_{\mathbf{q}_1 j_1}t} + \bar{n}_{\mathbf{q}_1 j_1} e^{i\omega_{\mathbf{q}_1 j_1}t}\right]$$

$$\times\left[(\bar{n}_{\mathbf{q}_2 j_2}+1)e^{-i\omega_{\mathbf{q}_2 j_2}t} + \bar{n}_{\mathbf{q}_2 j_2} e^{i\omega_{\mathbf{q}_2 j_2}t}\right]$$

$$\times\, \delta_{\mathbf{q}_1-\mathbf{q}_3}\,\delta_{\mathbf{q}_2-\mathbf{q}_4}\,\delta_{j_1 j_3}\,\delta_{j_2 j_4}\,dt \tag{2.54}$$

Performing the integration over the time coordinate t we find for J_4^C

$$J_4^c = 2\Big[(\bar{n}_{\mathbf{q}_1 j_1}+1)(\bar{n}_{\mathbf{q}_2 j_2}+1)\,\delta(\omega-\omega_{\mathbf{q}_1 j_1}-\omega_{\mathbf{q}_2 j_2})$$

$$+(\bar{n}_{\mathbf{q}_1 j_1}+1)\,\bar{n}_{\mathbf{q}_2 j_2}\,\delta(\omega-\omega_{\mathbf{q}_1 j_1}+\omega_{\mathbf{q}_2 j_2})$$

$$+\bar{n}_{\mathbf{q}_1 j_1}(\bar{n}_{\mathbf{q}_2 j_2}+1)\,\delta(\omega+\omega_{\mathbf{q}_1 j_1}-\omega_{\mathbf{q}_2 j_2})$$

$$+\bar{n}_{\mathbf{q}_1 j_1}\, n_{\mathbf{q}_2 j_2}\,\delta(\omega+\omega_{\mathbf{q}_1 j_1}+\omega_{\mathbf{q}_2 j_2})\Big]$$

$$\times\, \delta_{\mathbf{q}_1-\mathbf{q}_3}\,\delta_{\mathbf{q}_2-\mathbf{q}_4}\,\delta_{j_1 j_3}\,\delta_{j_2 j_4} \tag{2.55}$$

Substituting Eq. (2.55) into Eq. (2.17) we can write the final form for $S_4^C(\underset{\sim}{q},\omega)$ as

$$
\begin{aligned}
S_4^C(\underset{\sim}{q},\omega) = {} & \left(\frac{1}{2!}\right)^2 N \left(\frac{\hbar}{2NM}\right)^2 \sum_{\substack{\underset{\sim}{q}_1, \underset{\sim}{q}_2 \\ j_1, j_2}} \frac{|\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}_1 j_1}|^2 \, |\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}_2 j_2}|^2}{\omega_{\underset{\sim}{q}_1 j_1}\,\omega_{\underset{\sim}{q}_2 j_2}} \\
& \times \Delta(-\underset{\sim}{q}+\underset{\sim}{q}_1+\underset{\sim}{q}_2) \Big[(\bar{n}_{\underset{\sim}{q}_1 j_1}+1)(\bar{n}_{\underset{\sim}{q}_2 j_2}+1) \\
& \times \delta(\omega-\omega_{\underset{\sim}{q}_1 j_1}-\omega_{\underset{\sim}{q}_2 j_2}) \\
& + \bar{n}_{\underset{\sim}{q}_1 j_1}(\bar{n}_{\underset{\sim}{q}_2 j_2}+1)\,\delta(\omega+\omega_{\underset{\sim}{q}_1 j_1}-\omega_{\underset{\sim}{q}_2 j_2}) \\
& + (\bar{n}_{\underset{\sim}{q}_1 j_1}+1)\,\bar{n}_{\underset{\sim}{q}_2 j_2}\,\delta(\omega-\omega_{\underset{\sim}{q}_1 j_1}+\omega_{\underset{\sim}{q}_2 j_2}) \\
& + \bar{n}_{\underset{\sim}{q}_1 j_1}\,\bar{n}_{\underset{\sim}{q}_2 j_2}\,\delta(\omega+\omega_{\underset{\sim}{q}_1 j_1}+\omega_{\underset{\sim}{q}_2 j_2}) \Big]
\end{aligned}
\tag{2.56}
$$

3.0 DERIVATION OF THE PHONON-LIMITED RESISTIVITY OF METALS (ρ)

As mentioned before at the end of Section 2, we now present the derivation of the contributions to ρ from the harmonic, QS, DW and MP parts of $S(\underset{\sim}{q}, \omega)$ derived by the Matrix element method. We also summarize the contributions to ρ from the CS, W and I as obtained by Shukla and Muller using the Green function method.

Substituting the various parts of $S(\underset{\sim}{q}, \omega)$ (Eqs. (2.8), (2.9) and (2.10)) into the resistivity formula as given by Eq. (2.2) we obtain

$$\rho(T) = \rho_2(T) + \rho_3(T) + \rho_4(T) \tag{3.1}$$

where $\rho_2(T)$, $\rho_3(T)$ and $\rho_4(T)$ represent the contributions from 2, 3 and 4 displacement operators respectively. In the next few subsections we present the derivations of $\rho_2(T)$, $\rho_4(T)$ etc.

3.1 DERIVATION OF $\rho_2(T)$

The expression for $\rho_2(T)$ is obtained by substituting Eq. (2.28a) into Eq. (2.2), i.e.,

$$\rho_2(T) = [\rho_2(T)]_0 + [\rho_2(T)]_1 + [\rho_2(T)]_2$$

where

$$[\rho_2(T)]_0 = C \int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|\, |W(|\underset{\sim}{q}|)|^2 \int_{-\infty}^{+\infty} d\omega \frac{\beta\omega}{(e^{\beta\hbar\omega}-1)} [S_2(\underset{\sim}{q},\omega)]_0 \tag{3.2}$$

$$[\rho_2(T)]_1 = C \int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|\, |W(|\underset{\sim}{q}|)|^2 \int_{-\infty}^{+\infty} d\omega \frac{\beta\omega}{(e^{\beta\hbar\omega}-1)} [S_2(\underset{\sim}{q},\omega)]_1 \tag{3.3}$$

$$[\rho_2(T)]_2 = C \int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|\, |W(|\underset{\sim}{q}|)|^2 \int_{-\infty}^{+\infty} d\omega \frac{\beta\omega}{(e^{\beta\hbar\omega}-1)} [S_2(\underset{\sim}{q},\omega)]_2 \tag{3.4}$$

Substituting for $[S_2(q,\omega)]_0$ from Eq. (2.36) into Eq. (3.2) we obtain:

$$[\rho_2(T)]_0 = \frac{C\hbar}{M} \int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|\, |W(|\underset{\sim}{q}|)|^2 \int_{-\infty}^{+\infty} d\omega \frac{\beta\omega}{(e^{\beta\hbar\omega}-1)}$$

$$\times \sum_j \frac{|\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}|^2}{\omega_{\underset{\sim}{q}j}} \Big[(\bar{n}_{\underset{\sim}{q}j}+1)\,\delta(\omega-\omega_{\underset{\sim}{q}j})$$

$$+ \bar{n}_{\underset{\sim}{q}j}\,\delta(\omega+\omega_{\underset{\sim}{q}j})\Big] \tag{3.5}$$

Performing the trivial integration over ω in Eq. (3.5) and noting that

$$\bar{n}_{\underset{\sim}{q}j} = \frac{1}{(e^{\beta\hbar\omega_{\underset{\sim}{q}j}}-1)} \tag{3.6}$$

and
$$(\bar{n}_{\underset{\sim}{q}j}+1) = \frac{1}{(1-e^{-\beta\hbar\omega_{\underset{\sim}{q}j}})} \tag{3.7}$$

we obtain

$$\rho_H(T) = \frac{c\hbar}{M}\sum_j \int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|\, |W(|\underset{\sim}{q}|)|^2 |\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}|^2$$
$$\times \frac{\beta}{(e^{\beta\hbar\omega_{\underset{\sim}{q}j}}-1)(1-e^{-\beta\hbar\omega_{\underset{\sim}{q}j}})} \tag{3.8}$$

Eq. (3.8) represents strictly the harmonic contribution to ρ and is identical to the usual formula employed by many authors in the numerical calculations of ρ viz., Eq. (2.1).

Next substituting Eq. (2.45) into Eq. (3.3) and performing the integration over ω we obtain the following expressions for $[\rho_2(T)]_1$

$$[\rho_2(T)]_1 = -\beta\left(\frac{\hbar}{2M}\right) 12c \sum_j \int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|\, |W(|\underset{\sim}{q}|)|^2 |\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}|$$

$$\times\left[\frac{\bar{n}_{\underset{\sim}{q}j}}{(1-e^{-\beta\hbar\omega_{\underset{\sim}{q}j}})} + \frac{\bar{n}_{\underset{\sim}{q}j}+1}{(e^{\beta\hbar\omega_{\underset{\sim}{q}j}}-1)}\right]$$

$$\times \sum_{\underset{\sim}{q}_1 j_1} V^4(\underset{\sim}{q}j, -\underset{\sim}{q}j, \underset{\sim}{q}_1 j_1, -\underset{\sim}{q}_1 j_1)$$

$$\times\left[\bar{n}_{\underset{\sim}{q}j}\bar{n}_{\underset{\sim}{q}_1 j_1} + (\bar{n}_{\underset{\sim}{q}j}+1)\bar{n}_{\underset{\sim}{q}_1 j_1} + \bar{n}_{\underset{\sim}{q}j}(\bar{n}_{\underset{\sim}{q}_1 j_1}+1) + (\bar{n}_{\underset{\sim}{q}j}+1)(\bar{n}_{\underset{\sim}{q}_1 j_1}+1)\right] \tag{3.9}$$

The Eq. (3.9) represents the quartic shift (QS) contribution to ρ. The expression (3.9) can be expressed explicitly in terms of the quartic phonon shift $\Delta^{4}_{qj}(\omega_{qj})$ (Shukla and Muller (1971)) and the thermal factors. This alternative form is given by

$$\rho_{QS}(T) = -\frac{\beta^2 c\hbar^2}{4M} \sum_j \int_{|q|<2k_F} d^3q\, |q|\, |W(|q|)|^2 |q\cdot \varepsilon_{qj}|^2 \times \Delta_{qj}(\omega_{qj}) \frac{\coth(\beta\hbar\omega_{qj}/2)}{\sinh^2(\beta\hbar\omega_{qj}/2)} \tag{3.10}$$

where $$\Delta_{qj}(\omega_{qj}) = \frac{12}{\hbar} \sum_{q_1 j_1} V^4(q_1 j_1, -q_1 j_1, qj, -qj)\, N_{q_1 j_1} \tag{3.11}$$

and $$N_{qj} = \coth(\beta\hbar\omega_{qj}/2) = (2\bar{n}_{qj}+1) \tag{3.12}$$

The contribution to ρ from $[\rho_2(T)]_2$ (Eq. (3.4)) term represent the CS and W contributions which have been derived by Shukla and Muller (1979) using the Green function method. The summarized version of these contributions are:

$$\rho_{CS}(T) = -\frac{\beta^2 c\hbar^2}{4M} \sum_j \int_{|q|<2k_F} d^3q\, |q|\, |W(|q|)|^2 |q\cdot \varepsilon_{qj}|^2 \times \Delta^3_{qj}(\omega_{qj}) \frac{\coth(\beta\hbar\omega_{qj}/2)}{\sinh^2(\beta\hbar\omega_{qj}/2)} \tag{3.13}$$

$$\rho_W(T) = \frac{\beta c\hbar}{M} \sum_j \int_{|q|<2k_F} d^3q\, |q|\, |W(|q|)|^2 \frac{|q\cdot \varepsilon_{qj}|^2}{\omega_{qj}} W_{qj}(\omega_{qj}) \tag{3.14}$$

where

$$\Delta^{3}_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) = \frac{18}{\hbar^2} \sum_{\substack{q_1 q_2 \\ j_1 j_2}} |V^3(-\underset{\sim}{q}j, \underset{\sim}{q}_1 j_1, \underset{\sim}{q}_2 j_2)|^2$$

$$\times P\left[(N_{\underset{\sim}{q}_1 j_1} + N_{\underset{\sim}{q}_2 j_2}) \frac{(\omega_{\underset{\sim}{q}_1 j_1} + \omega_{\underset{\sim}{q}_2 j_2})}{\omega_{\underset{\sim}{q}j}^2 - (\omega_{\underset{\sim}{q}_1 j_1} + \omega_{\underset{\sim}{q}_2 j_2})^2}\right.$$

$$\left. + (N_{\underset{\sim}{q}_2 j_2} - N_{\underset{\sim}{q}_1 j_1}) \frac{(\omega_{\underset{\sim}{q}_1 j_1} - \omega_{\underset{\sim}{q}_2 j_2})}{\omega_{\underset{\sim}{q}j}^2 - (\omega_{\underset{\sim}{q}_1 j_1} - \omega_{\underset{\sim}{q}_2 j_2})^2}\right] \quad (3.15)$$

$$W_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) = \frac{18}{\hbar^2} \sum_{\substack{q_1 q_2 \\ j_1 j_2}} |V^3(-\underset{\sim}{q}j, \underset{\sim}{q}_1 j_1, \underset{\sim}{q}_2 j_2)|^2$$

$$\times \left[(N_{\underset{\sim}{q}_1 j_1} + N_{\underset{\sim}{q}_2 j_2}) \frac{(\omega_{\underset{\sim}{q}_1 j_1} + \omega_{\underset{\sim}{q}_2 j_2})}{(\omega_{\underset{\sim}{q}j} - \omega_{\underset{\sim}{q}_1 j_1} - \omega_{\underset{\sim}{q}_2 j_2})^2}\right.$$

$$\times \frac{1}{(1 - e^{\beta\hbar(\omega_{\underset{\sim}{q}_1 j_1} + \omega_{\underset{\sim}{q}_2 j_2})})(e^{-\beta\hbar(\omega_{\underset{\sim}{q}_1 j_1} + \omega_{\underset{\sim}{q}_2 j_2})} - 1)}$$

$$+ (N_{\underset{\sim}{q}_2 j_2} - N_{\underset{\sim}{q}_1 j_1}) \frac{(\omega_{\underset{\sim}{q}_1 j_1} - \omega_{\underset{\sim}{q}_2 j_2})}{(\omega_{\underset{\sim}{q}j} - \omega_{\underset{\sim}{q}_1 j_1} + \omega_{\underset{\sim}{q}_2 j_2})^2}$$

$$\left.\times \frac{1}{(1 - e^{\beta\hbar(\omega_{\underset{\sim}{q}_1 j_1} - \omega_{\underset{\sim}{q}_2 j_2})})(e^{-\beta\hbar(\omega_{\underset{\sim}{q}_1 j_1} - \omega_{\underset{\sim}{q}_2 j_2})} - 1)}\right] \quad (3.16)$$

and the symbol P in front of the square bracket in Eq. (3.15) represent the Principal part.

We also present the contribution to ρ from $\rho_3(T)$ the I contribution derived by Shukla and Muller (1979). This contribution is given by

$$\rho_I(T) = \frac{-i\,3\beta N c}{\hbar}\left(\frac{\hbar}{2NM}\right)^{1/2} \sum_j \int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|\, |W(|\underset{\sim}{q}|)|^2\, I_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) \quad (3.17)$$

where

$$I_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) = \sum_{\substack{\underset{\sim}{q}_1 j_1 \\ \underset{\sim}{q}_2 j_2}} \Delta(-\underset{\sim}{q}+\underset{\sim}{q}_1+\underset{\sim}{q}_2) \frac{(\underset{\sim}{q}\cdot\underset{\sim}{\xi}_{\underset{\sim}{q}j})(\underset{\sim}{q}\cdot\underset{\sim}{\xi}_{\underset{\sim}{q}_1 j_1})(\underset{\sim}{q}\cdot\underset{\sim}{\xi}_{\underset{\sim}{q}_2 j_2})}{(\omega_{\underset{\sim}{q}j}\,\omega_{\underset{\sim}{q}_1 j_1}\,\omega_{\underset{\sim}{q}_2 j_2})^{1/2}}$$

$$\times V^3(-\underset{\sim}{q}_1 j_1, -\underset{\sim}{q}_2 j_2, \underset{\sim}{q}j)\,\omega_{\underset{\sim}{q}j} \Bigg[\frac{(N_{\underset{\sim}{q}_1 j_1}+N_{\underset{\sim}{q}_2 j_2})(\omega_{\underset{\sim}{q}_1 j_1}+\omega_{\underset{\sim}{q}_2 j_2})}{(\omega_{\underset{\sim}{q}_1 j_1}+\omega_{\underset{\sim}{q}_2 j_2})^2-\omega_{\underset{\sim}{q}j}^{\,2}}$$

$$\times \left\{ \operatorname{cosech}^2\left(\frac{\beta\hbar}{2}(\omega_{\underset{\sim}{q}_1 j_1}+\omega_{\underset{\sim}{q}_2 j_2})\right) - \operatorname{cosech}^2\left(\frac{\beta\hbar}{2}\omega_{\underset{\sim}{q}j}\right) \right\}$$

$$+ \frac{(N_{\underset{\sim}{q}_2 j_2}-N_{\underset{\sim}{q}_1 j_1})(\omega_{\underset{\sim}{q}_1 j_1}-\omega_{\underset{\sim}{q}_2 j_2})}{(\omega_{\underset{\sim}{q}_1 j_1}-\omega_{\underset{\sim}{q}_2 j_2})^2-\omega_{\underset{\sim}{q}j}^{\,2}}$$

$$\times \left\{ \operatorname{cosech}^2\left(\frac{\beta\hbar}{2}(\omega_{\underset{\sim}{q}_1 j_1}-\omega_{\underset{\sim}{q}_2 j_2})\right) - \operatorname{cosech}^2\left(\frac{\beta\hbar}{2}\omega_{\underset{\sim}{q}j}\right) \right\} \Bigg] \tag{3.18}$$

3.2 DERIVATION OF $\rho_4(T)$

From Section 2.0 we can write $S_4(\underset{\sim}{q}, \omega)$ as

$$S_4(\underset{\sim}{q}, \omega) = 2S_4^A(\underset{\sim}{q}, \omega) + S_4^c(\underset{\sim}{q}, \omega) \tag{3.19}$$

Substituting Eq. (3.19) into Eq. (2.2) we obtain the following expression for the contribution to ρ from $S_4(\underset{\sim}{q}, \omega)$

$$\rho_4(T) = 2\rho_4^A(T) + \rho_4^c(T) \tag{3.20}$$

where

$$\rho_4^A(T) = c\int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|\, |W(|\underset{\sim}{q}|)|^2 \int_{-\infty}^{+\infty} \frac{\beta\omega}{(e^{\beta\hbar\omega}-1)} S_4^A(\underset{\sim}{q}, \omega)\, d\omega \tag{3.21}$$

$$\rho_4^B(T) = c\int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|\, |W(|\underset{\sim}{q}|)|^2 \int_{-\infty}^{+\infty} \frac{\beta\omega}{(e^{\beta\hbar\omega}-1)} S_4^c(\underset{\sim}{q}, \omega)\, d\omega \tag{3.22}$$

Substitution for $S_4^A(\underset{\sim}{q}, \omega)$ from Eq. (2.50) into Eq.(3.21) and integrating over ω, we obtain.

$$\rho_4^A(T) = -\frac{6}{3!} N \left(\frac{\hbar}{2NM}\right)^2 \beta c \int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|\, |W(|\underset{\sim}{q}|)|^2 |\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}|^2$$

$$\times\ \bar{n}_{\underset{\sim}{q}j}(\bar{n}_{\underset{\sim}{q}j}+1) \sum_{\underset{\sim}{q}_1 j_1} \frac{|\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}_1 j_1}|^2}{\omega_{\underset{\sim}{q}_1 j_1}} (2\bar{n}_{\underset{\sim}{q}_1 j_1}+1) \tag{3.23}$$

Now, we know that the factor

$$D(\underset{\sim}{q}) = \left(\frac{\hbar}{2NM}\right) \sum_{\underset{\sim}{q}_1 j_1} \frac{|\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}_1 j_1}|^2}{\omega_{\underset{\sim}{q}_1 j_1}} (2\bar{n}_{\underset{\sim}{q}_1 j_1}+1) \tag{3.24}$$

is the well known expression for the Debye-Waller factor [Pines (1964)], hence $2\rho_4^A(T)$ represents the DW contribution to ρ and we can rearrange Eq. (3.23) in the following form:

$$2\rho_4^A(T) = \rho_{DW} = -\frac{1}{2}\frac{ch}{M}\beta\int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\,|\underset{\sim}{q}|\,|W(|\underset{\sim}{q}|)|^2\,|\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}|^2$$

$$\times\,\bar{n}_{\underset{\sim}{q}j}(\bar{n}_{\underset{\sim}{q}j}+1)\,D(\underset{\sim}{q}) \tag{3.25}$$

To derive the $\rho_4^C(T)$ contribution to ρ, first we substitute Eq. (2.56) into Eq. (3.22) to obtain:

$$\rho_4^C(T) = \left(\frac{1}{2!}\right)^2 N\left(\frac{\hbar}{2NM}\right)^2 2c\int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\,|\underset{\sim}{q}|\,|W(|\underset{\sim}{q}|)|^2$$

$$\times\sum_{\substack{q_1,q_2\\ j_1,j_2}}\frac{|\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{q_1j_1}|^2|\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{q_2j_2}|^2}{\omega_{\underset{\sim}{q}_1j_1}\,\omega_{\underset{\sim}{q}_2j_2}}\,\Delta(-\underset{\sim}{q}+\underset{\sim}{q}_1+\underset{\sim}{q}_2)$$

$$\times\int_{-\infty}^{+\infty} d\omega\,\frac{\beta\omega}{(e^{\beta\hbar\omega}-1)}\Big[(\bar{n}_{\underset{\sim}{q}_1j_1}+1)(\bar{n}_{\underset{\sim}{q}_2j_2}+1)\,\delta(\omega-\omega_{\underset{\sim}{q}_1j_1}-\omega_{\underset{\sim}{q}_2j_2})$$

$$+\,\bar{n}_{\underset{\sim}{q}_1j_1}(\bar{n}_{\underset{\sim}{q}_2j_2}+1)\,\delta(\omega+\omega_{\underset{\sim}{q}_1j_1}-\omega_{\underset{\sim}{q}_2j_2})$$

$$+\,(\bar{n}_{\underset{\sim}{q}_1j_1}+1)\,\bar{n}_{\underset{\sim}{q}_2j_2}\,\delta(\omega-\omega_{\underset{\sim}{q}_1j_1}+\omega_{\underset{\sim}{q}_2j_2})$$

$$+\,\bar{n}_{\underset{\sim}{q}_1j_1}\,\bar{n}_{\underset{\sim}{q}_2j_2}\,\delta(\omega+\omega_{\underset{\sim}{q}_1j_1}+\omega_{\underset{\sim}{q}_2j_2})\Big] \tag{3.26}$$

The correction to $\rho(T)$ from $\rho_4^C(T)$ is the contribution from the first term of the multi-phonon series and will be referred to as $\rho_{MP}(T)$. Performing the integration over ω in Eq. (3.26) we can write $\rho_{MP}(T)$ as

$$\rho_{MP}(T) = \frac{1}{8}\,\frac{c\hbar^2}{M^2 N}\,\beta \int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|\, |W(|\underset{\sim}{q}|)|^2 M(\underset{\sim}{q}) \tag{3.27}$$

where

$$M(\underset{\sim}{q}) = \sum_{\substack{q_1 q_2 \\ j_1 j_2}} \frac{|\underline{q}\cdot \underset{\sim}{\varepsilon}_{\underline{q}_1 j_1}|^2\, |\underline{q}\cdot \underset{\sim}{\varepsilon}_{\underline{q}_2 j_2}|^2}{\omega_{\underline{q}_1 j_1}\,\omega_{\underline{q}_2 j_2}}\, \Delta(-\underline{q}+\underline{q}_1+\underline{q}_2)$$

$$\times \left[\frac{(\bar{n}_{\underline{q}_1 j_1}+1)(\bar{n}_{\underline{q}_2 j_2}+1)(\omega_{\underline{q}_1 j_1}+\omega_{\underline{q}_2 j_2})}{(e^{\beta\hbar(\omega_{\underline{q}_1 j_1}+\omega_{\underline{q}_2 j_2})}-1)} \right.$$

$$+ \frac{\bar{n}_{\underline{q}_1 j_1}(\bar{n}_{\underline{q}_2 j_2}+1)(\omega_{\underline{q}_2 j_2}-\omega_{\underline{q}_1 j_1})}{(e^{\beta\hbar(\omega_{\underline{q}_2 j_2}-\omega_{\underline{q}_1 j_1})}-1)}$$

$$+ \frac{(\bar{n}_{\underline{q}_1 j_1}+1)\bar{n}_{\underline{q}_2 j_2}(\omega_{\underline{q}_1 j_1}-\omega_{\underline{q}_2 j_2})}{(e^{\beta\hbar(\omega_{\underline{q}_1 j_1}-\omega_{\underline{q}_2 j_2})}-1)}$$

$$\left. + \frac{\bar{n}_{\underline{q}_1 j_1}\bar{n}_{\underline{q}_2 j_2}(-\omega_{\underline{q}_1 j_1}-\omega_{\underline{q}_2 j_2})}{(e^{\beta\hbar(-\omega_{\underline{q}_1 j_1}-\omega_{\underline{q}_2 j_2})}-1)} \right] \tag{3.28}$$

4. THE HIGH TEMPERATURE LIMIT OF ρ TO $O(T^2)$

The expressions for the various contributions to ρ given in Section 3. contain the thermal factors $(\bar{n}_{\underset{\sim}{q}j})$. In the high temperature limit (i.e., $T > \Theta_D$, the Debye temperature) $\beta\hbar\omega_{\underset{\sim}{q}j} < 1$, therefore it is possible to expand the thermal factors arising in these epressions in powers of T.

In the high temperature limit, the thermal factor

$$\bar{n}_{\underset{\sim}{q}j} = \frac{1}{(e^{\beta\hbar\omega_{\underset{\sim}{q}j}}-1)} \approx \frac{1}{\beta\hbar\omega_{\underset{\sim}{q}j}}$$

and

$$\bar{n}_{\underset{\sim}{q}j}+1 = \frac{1}{(1-e^{-\beta\hbar\omega_{\underset{\sim}{q}j}})} \approx \frac{1}{\beta\hbar\omega_{\underset{\sim}{q}j}}$$

so that in the high temperature limit ρ_H given by Eqs. (3.8) becomes

$$\rho_H(T) = \frac{C}{\beta\hbar M}\sum_j \int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|\, |W(|\underset{\sim}{q}|)|^2 \frac{|\hat{\underset{\sim}{q}}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}|^2}{\omega_{\underset{\sim}{q}j}^{\,2}} \tag{4.1}$$

Also in the high temperature limit the other thermal factors are expanded as follows:

$$N_{\underset{\sim}{q}j} = \coth\left(\frac{\beta\hbar}{2}\omega_{\underset{\sim}{q}j}\right) \approx \frac{2}{\beta\hbar\omega_{\underset{\sim}{q}j}}$$

$$\sinh^2\left(\frac{\beta\hbar}{2}\omega_{\underset{\sim}{q}j}\right) \approx \left(\frac{\beta\hbar}{2}\omega_{\underset{\sim}{q}j}\right)^2$$

and

$$\operatorname{cosech}^2\left(\frac{\beta\hbar}{2}\omega_{\underset{\sim}{q}j}\right) \approx \left(\frac{2}{\beta\hbar\omega_{\underset{\sim}{q}j}}\right)^2$$

Thus, the contribution to ρ from the cubic and quartic shifts as given by Eqs. (3.13), (3.15) and (3.10) and (3.11), respectively, can be simplified to the following:

$$\rho_{CS}(T) = \frac{-2c}{\beta\hbar M} \sum_{j} \int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|\, |W(|\underset{\sim}{q}|)|^2 \frac{|\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}|^2}{\omega_{\underset{\sim}{q}j}^{3}}\, \Delta^3_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) \tag{4.2}$$

where

$$\Delta^3_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) = \frac{36\lambda}{\beta\hbar^3} \sum_{\substack{\underset{\sim}{q}_1\underset{\sim}{q}_2\\ j_1 j_2}} |V^3(-\underset{\sim}{q}j, \underset{\sim}{q}_1 j_1, \underset{\sim}{q}_2 j_2)|^2$$

$$\times \frac{1}{\omega_{\underset{\sim}{q}_1 j_1}\omega_{\underset{\sim}{q}_2 j_2}}\, P\left[\frac{(\omega_{\underset{\sim}{q}_1 j_1}+\omega_{\underset{\sim}{q}_2 j_2})^2}{\omega^2_{\underset{\sim}{q}j}-(\omega_{\underset{\sim}{q}_1 j_1}+\omega_{\underset{\sim}{q}_2 j_2})^2} - \frac{(\omega_{\underset{\sim}{q}_1 j_1}-\omega_{\underset{\sim}{q}_2 j_2})^2}{\omega^2_{\underset{\sim}{q}j}-(\omega_{\underset{\sim}{q}_1 j_1}-\omega_{\underset{\sim}{q}_2 j_2})^2}\right] \tag{4.3}$$

and

$$\rho_{QS}(T) = \frac{-2c}{\beta\hbar M} \sum_{j} \int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|\, |W(|\underset{\sim}{q}|)|^2 \frac{|\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}|^2}{\omega_{\underset{\sim}{q}j}^{3}}\, \Delta^4_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) \tag{4.4}$$

where

$$\Delta^4_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) = \frac{24}{\beta\hbar^2} \sum_{\underset{\sim}{q}_1 j_1} \frac{V^4(\underset{\sim}{q}_1 j_1, -\underset{\sim}{q}_1 j_1, \underset{\sim}{q}j, -\underset{\sim}{q}j)}{\omega_{\underset{\sim}{q}_1 j_1}} \tag{4.5}$$

The contribution to ρ from the phonon width as given by Eqs. (3.14) and (3.16), reduces in the high temperature limit to the following:

$$\rho_{WD}(T) = \frac{\beta\hbar c}{M} \sum_{j} \int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|\, |W(|\underset{\sim}{q}|)|^2 \frac{|\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}|^2}{\omega_{\underset{\sim}{q}j}}\, W_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) \tag{4.6}$$

where

$$W_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) = \frac{36}{\beta^3\hbar^5} \sum_{\substack{\underset{\sim}{q}_1\underset{\sim}{q}_2\\ j_1 j_2}} |V^3(-\underset{\sim}{q}j, \underset{\sim}{q}_1 j_1, \underset{\sim}{q}_2 j_2)|^2$$

$$\times \left[\frac{1}{\omega_{\underset{\sim}{q}_1 j_1}\omega_{\underset{\sim}{q}_2 j_2}(\omega_{\underset{\sim}{q}j}-\omega_{\underset{\sim}{q}_1 j_1}-\omega_{\underset{\sim}{q}_2 j_2})^2} + \frac{1}{\omega_{\underset{\sim}{q}_1 j_1}\omega_{\underset{\sim}{q}_2 j_2}(\omega_{\underset{\sim}{q}j}-\omega_{\underset{\sim}{q}_1 j_1}+\omega_{\underset{\sim}{q}_2 j_2})^2}\right] \tag{4.7}$$

Similarly from Eqs. (3.17) and (3.18) the interference term contribution to ρ can be reduced in the high temperature limit to the form

$$\rho_I(T) = \frac{-i\,3\beta N c}{\hbar}\left(\frac{\hbar}{2NM}\right)^{1/2} \sum_j \int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|\, |W(|\underset{\sim}{q}|)|^2\, I_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) \tag{4.8}$$

where

$$I_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) = -2\left(\frac{2}{\beta\hbar}\right)^3 \sum_{\substack{q_1\, q_2\\ j_1\, j_2}} \Delta(-\underset{\sim}{q}+\underset{\sim}{q}_1+\underset{\sim}{q}_2)\, V^3(-\underset{\sim}{q}_1 j_1, -\underset{\sim}{q}_2 j_2, \underset{\sim}{q}j)$$

$$\times \frac{(\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j})(\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{q_1 j_1})(\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{q_2 j_2})}{(\omega_{\underset{\sim}{q}j}\,\omega_{\underset{\sim}{q}_1 j_1}\,\omega_{\underset{\sim}{q}_2 j_2})^{1/2}} \tag{4.9}$$

Finally the Debye-Waller and multi-phonon contributions to ρ as given by Eqs. (3.25), (3.24) and (3.27) and (3.28), respectively, reduce to the following form in the high temperature limit.

$$\rho_{DW}(T) = \frac{-1}{2}\,\frac{c}{\beta M^2 N} \sum_j \int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|\, |W(|\underset{\sim}{q}|)|^2\, \frac{|\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}|}{\omega_{\underset{\sim}{q}j}^{\,2}}\, D(\underset{\sim}{q}) \tag{4.10}$$

where $$D(\underset{\sim}{q}) = \frac{2}{\beta\hbar} \sum_{\underset{\sim}{q}_1 j_1} \frac{|\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{q_1 j_1}|^2}{\omega_{\underset{\sim}{q}_1 j_1}^{\,2}} \tag{4.11}$$

$$\rho_{MP}(T) = \frac{c\hbar^2}{8M^2N}\,\beta \int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|\, |W(|\underset{\sim}{q}|)|^2\, M(\underset{\sim}{q}) \tag{4.12}$$

where

$$M(\underset{\sim}{q}) = \frac{4}{\beta^3\hbar^3} \sum_{\substack{q_1\, q_2\\ j_1\, j_2}} \frac{|\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{q_1 j_1}|^2\, |\underset{\sim}{q}\cdot\underset{\sim}{\varepsilon}_{q_2 j_2}|^2}{\omega_{\underset{\sim}{q}_1 j_1}^{\,2}\, \omega_{\underset{\sim}{q}_2 j_2}^{\,2}}\, \Delta(-\underset{\sim}{q}+\underset{\sim}{q}_1+\underset{\sim}{q}_2) \tag{4.13}$$

5. NUMERICAL CALCULATIONS

Our main objective is to calculate the various contributions to ρ to the $O(T^2)$ in the high temperature limit. In this section, we will outline the numerical calculation of the two general types of integrals for ρ, which are representative of all types of integrals arising in Section 4. The following sections contain the numerical calculations of the individual contributions to ρ.

From Section 4, we see that the following two types of integrals are to be evaluated.

$$\rho_A(T) = c \int_{|\underset{\sim}{q}|<2k_F} d^3q \, |\underset{\sim}{q}| \, |W(|\underset{\sim}{q}|)|^2 \, |\underset{\sim}{q} \cdot \underset{\sim}{\varepsilon}_{qj}|^2 \, f(\omega_{\underset{\sim}{q}j}) \tag{5.1}$$

and

$$\rho_B(T) = c \int_{|\underset{\sim}{q}|<2k_F} d^3q \, |\underset{\sim}{q}| \, |W(|\underset{\sim}{q}|)|^2 \, g(\omega_{\underset{\sim}{q}j}, \underset{\sim}{\varepsilon}_{qj}) \tag{5.2}$$

where the function $f(\omega_{\underset{\sim}{q}j})$ arises in the contributions to ρ from the harmonic term, the cubic chift (CS), the quartic shift (QS), the width (W) and the Debye-Waller (DW) factor. The function $g(\omega_{\underset{\sim}{q}j}, \underset{\sim}{\varepsilon}_{qj})$ arises in the contributions to ρ from the multiphonon (MP) and the interference (I) terms. The complete expressions for the functions $f(\omega_{\underset{\sim}{q}j})$ and $g(\omega_{\underset{\sim}{q}j}, \underset{\sim}{\varepsilon}_{qj})$ can be found in Section 4.

In order to compute ρ from Eqs. (5.1) or (5.2), we need to know $W(|\underset{\sim}{q}|)$, $\omega_{\underset{\sim}{q}j}$ for wave-vectors $\underset{\sim}{q}$ up to a sphere of radius $2k_F$. But $|\underset{\sim}{q}| < 2k_F$ for all the points on the boundary of the first Brillouin zone (F.B.Z.) and $(\omega_{\underset{\sim}{q}j}, \underset{\sim}{\varepsilon}_{qj})$ are normally known in the F.B.Z. These points out to a radius of $2k_F$, can be generated by the addition of reciprocal lattice vectors ($\underset{\sim}{\tau}$) to the wave vector $\underset{\sim}{q}$, under consideration, such that the resulting vectors have a magnitude less than $2k_F$. The periodic property of $\omega_{\underset{\sim}{q}j}$ and $\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}$ gives $\omega_{(\underset{\sim}{q}+\underset{\sim}{\tau})j} = \omega_{\underset{\sim}{q}j}$ and $\underset{\sim}{\varepsilon}_{(\underset{\sim}{q}+\underset{\sim}{\tau})j} = \pm \underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}$. The negative sign of $\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}$ is unimportant because in the expressions for ρ from the various contributions as given by Eqs. (4.1) to (4.13) only the square of $\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}$ dotted with the new wave vector arises. Also the new wave vector is assigned the same weight as the wave vector that produced it. The weights are obtained from the 48 symmetry transformations of a cube, taking into account the sharing factors if the wave vector lies on the boundary of the F. B. Z.

In our computer program which evaluates the expressions (5.1) and (5.2), we first generate the wave vectors for a step length (L = 20), which gives us a mesh size of 70 odd wave vectors in the irreducible 1/48 th portion of the F.B.Z. The wave vectors $\underset{\sim}{q} = \left(\frac{2\pi}{a}\right)\left(\frac{\vec{p}}{L}\right)$, are generated from the boundaries of the F. B. Z. defined by $p_x + p_y \leq L$, $p_y + p_z \leq L$, $p_z + p_x \leq L$ and $0 \leq p_x \leq p_y \leq p_z$, where p_x, p_y, p_z are odd integers and a is the lattice constant.

Next we evaluate the elements of the Dynamical matrix (Shukla (1966)), using the first thirteen neighbour force constants in real space. The force constants used in our calculations are those obtained by Shukla and Taylor (1975) for Na and K at 0°K volume. Once we have the Dynamical matrix, we can obtain $\omega_{\underset{\sim}{q}j}$ and $\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}$ by diagonalization (Jacobi method).

The function $W(|\underset{\sim}{q}|)$ is the screened electron-ion pseudo-potential form factor and the values for Na and K at 0°K volume have been taken from Shukla and Taylor (1975).

Now to assess the numerical accuracy of the integrations in Eqs. (5.1) and (5.2), we introduce the following test integrals (Shukla and Taylor (1975)), which are obtained by setting $f(\omega_{\underset{\sim}{q}j})$, $g(\omega_{\underset{\sim}{q}j}, \underset{\sim}{\varepsilon}_{\underset{\sim}{q}j})$ and $W(|\underset{\sim}{q}|)$ equal to unity in Eqs. (5.1) and (5.2), respectively.

$$I = \sum_j \int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|\, |\underset{\sim}{q}\cdot \underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}|^2$$

$$J = \int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|$$

The integral I serves the purpose of checking the transformation property of the eigenvectors in the full calculation, whereas the integrals I and J both serve the purpose of checking the mesh size of the wave vectors and the correctness of their weight in the full calculation.

The test integrals I and J can be evaluated exactly. Since $\sum_j e_\alpha(\underset{\sim}{q}j)e_\beta(\underset{\sim}{q}j) = \delta_{\alpha\beta}$, where $e_\alpha(\underset{\sim}{q}j), e_\beta(\underset{\sim}{q}j)$ (α or β = x, y, z) are the components of $\underset{\sim}{\varepsilon}(\underset{\sim}{q}j)$,

$$\begin{aligned}\sum_j |\underset{\sim}{q}\cdot \underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}|^2 &= \sum_{\alpha\beta} q_\alpha q_\beta \sum_j e_\alpha(\underset{\sim}{q}j)\, e_\beta(\underset{\sim}{q}j) \\ &= \sum_{\alpha\beta} q_\alpha q_\beta \delta_{\alpha\beta} \\ &= |\underset{\sim}{q}|^2\end{aligned}$$

we have on exact integration,

$$I = \int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}|^3 = \frac{4\pi(2k_F)^6}{6}$$

$$J = \int_{|\underset{\sim}{q}|<2k_F} d^3\underset{\sim}{q}\, |\underset{\sim}{q}| = 16\pi k_F^4$$

Since we know these integrals exactly, we can see how well our program reproduces these integrals for a given mesh size. We have found that for L = 20, I and J are numerically calculated to within 0.1% of the exact value.

Although different weighting factors involving functions of $\omega_{\underset{\sim}{q}j}$, $\underset{\sim}{\epsilon}_{\underset{\sim}{q}j}$ and $\underset{\sim}{q}$ are contained in the actual calculation of ρ, they are not expected to change the convergence of ρ with a change in the mesh size.

The harmonic contribution ρ_H as given by Eq. (4.1) has been computed by the above method for Na and K and the results are given in Tables 1-14.

We see, from section 4, that the resistivity integrand ($I\rho$) contains W ($|\underset{\sim}{q}|$), which is known in reciprocal space. The anharmonic coefficients are obtained from a two body potential $\phi(r)$, which consists of a direct coulomb contribution of the ions and the electron-ion interaction. Therefore, the factors arising in the anharmonic coefficient in Eqs. (4.3), (4.5), (4.7) and (4.9) must be computed in the reciprocal space. Clearly, a natural choice for this type of calculation would be to compute the contributions to the various terms in $I\rho$ from the electron-ion term in reciprocal space and the coulomb term contribution to the various terms in $I\rho$ in the real and reciprocal space, i.e., Ewald method (1921).

We shall now discuss the various contributions to ρ as computed exactly for DW, MP and QS and computed approximately for QS, CS, W and I. The two types of approximations used are the total Einstein and the partial Einstein, which are discussed in Section (5.4).

5.1. THE DEBYE-WALLER (DW) CONTRIBUTION TO THE PHONON-LIMITED RESISTIVITY OF METALS (ρ)

The numerical calculation of the contribution to ρ from the DW requires the numerical evaluation of the Bruillouin zone (B.Z.) sum $D(\underset{\sim}{q})$ given by Eq. (4.11). This sum can be expressed in terms of the tensor $S_{\alpha\beta}(n)$ defined by Shukla and Wilk (1974),

$$S_{\alpha\beta}(n) = \sum_{\underset{\sim}{q}_1 j_1} \frac{e_\alpha(\underset{\sim}{q}_1 j_1)\, e_\beta(\underset{\sim}{q}_1 j_1)\cos(\underset{\sim}{q}_1 \cdot \underset{\sim}{r}_n)}{\omega_{\underset{\sim}{q}_1 j_1}^2} \tag{5.3}$$

i.e.,

$$D(\underset{\sim}{q}) = \frac{2}{\beta\hbar} \sum_{\alpha\beta} \sum_{\underset{\sim}{q}_1 j_1} q_\alpha q_\beta \frac{e_\alpha(\underset{\sim}{q}_1 j_1)\, e_\beta(\underset{\sim}{q}_1 j_1)}{\omega^2_{\underset{\sim}{q}_1 j_1}}$$

$$= \frac{2}{\beta\hbar} \sum_{\alpha\beta} q_\alpha q_\beta S_{\alpha\beta}(0) \tag{5.4}$$

where α, β each is assigned the Cartesian indices x, y, z; $\underset{\sim}{r}_n = \frac{a}{2}(n_x, n_y, n_z)$ and for a b.c.c. lattice n_x, n_y, n_z are either all odd or all even integers.

The B.Z. sum $S_{\alpha\beta}(n)$ can be computed from the method described in Shukla and Wilk (1974).

We have computed $S_{\alpha\beta}(0)$ for a step length (L = 64) which gives a mesh size of 1632 wave vectors in the irreducible 1/48th portion of the F.B.Z. (Ir. F.B.Z.). For this mesh size the B.Z. sum $S_{\alpha\beta}(0)$ is accurately computed to an accuracy of 1.0%.

Once we have $S_{\alpha\beta}(0)$, for a given wave vector $\underset{\sim}{q}$, $D(\underset{\sim}{q})$ can be obtained from Eq. (5.4). Substituting these values of $D(\underset{\sim}{q})$ in Eq. (4.10), the resulting integrand can be integrated in exactly the same manner as described in Section 5. The DW factor contributions to ρ for Na and K are presented in Tables 1 and 2, respectively.

5.2 THE MULTI-PHONON (MP) CONTRIBUTION TO THE PHONON-LIMITED RESISTIVITY OF METALS (ρ)

For the numerical calculation of the contribution to ρ from the MP term as given by Eq. (4.12) we have to first calculate the complicated B.Z. sum given in Eq. (4.13). The function $M(\underset{\sim}{q})$ is complicated because the double sum $\underset{\sim}{q}_1$ and $\underset{\sim}{q}_2$ over the B.Z. are restricted by the delta (Δ) function $\Delta(-\underset{\sim}{q} + \underset{\sim}{q}_1 + \underset{\sim}{q}_2)$. Using the plane wave representation of the Δ function we can uncouple the sums over $\underset{\sim}{q}_1$ and $\underset{\sim}{q}_2$. This representation is given by

$$\Delta(-\underset{\sim}{q} + \underset{\sim}{q}_1 + \underset{\sim}{q}_2) = \frac{1}{N} \sum_n e^{i(-\underset{\sim}{q} + \underset{\sim}{q}_1 + \underset{\sim}{q}_2)\cdot \underset{\sim}{r}_n} \tag{5.5}$$

where N is the number of unit cells in the crystal and $\underset{\sim}{r}_n$ is the direct lattice vector. Substituting Eq. (5.5) into Eq. (4.13), rearranging the terms, M(q) can be written in terms of $S_{\alpha\beta}(n)$ in the following form

$$M(\underset{\sim}{q}) = \frac{4}{\beta \hbar^3 N} \sum_n \cos(\underset{\sim}{q}\cdot\underset{\sim}{r}_n) \left[\sum_{\alpha\beta} q_\alpha q_\beta S_{\alpha\beta}(n)\right]^2 \tag{5.6}$$

where $S_{\alpha\beta}(n)$ is defined by Eq. (5.3) and computed by the method described in Section 5.2 not only for n = 0 as before, but for a large number of direct b.c.c. lattice points (n). The sum over the direct lattice vectors ($\underset{\sim}{r}_n$) in Eq. (5.6) is taken out to 60 shells, where the percentage change due to the addition of the 60 th shell in $M(\underset{\sim}{q})$ is 0.05% for a wave vector $\underset{\sim}{q}$ near the origin and 0.2% for $\underset{\sim}{q}$ close to the surface of the B.Z.

The **numerical** values obtained in the above calculation for $M(\underset{\sim}{q})$ for different $\underset{\sim}{q}$ vectors are then employed in Eq. (4.12) in the numerical calculation of the necessary integral described previously in Section 5.

The numerical results obtained from this integral for the MP contribution to ρ for Na and K are presented in Tables 1 and 2, respectively.

5.3 INTRODUCTION TO THE ANHARMONIC CONTRIBUTIONS TO THE PHONON-LIMITED RESISTIVITY OF METALS (ρ)

Examining the anharmonic contributions to ρ from the CS, QS, W and I processes, as given by Eqs. (4.3), (4.5), (4.7) and (4.9), respectively, we note that their numerical calculation requires the knowledge of the Fourier transform of the anharmonic force constant. In general, this transform is given by Born and Huang (1954) (Shukla and Wilk (1974)).

$$V^m(\underset{\sim}{q}_1 j_1, \cdots \underset{\sim}{q}_m j_m) = \frac{1}{m!} N^{1-m/2} \Delta(\underset{\sim}{q}_1 + \cdots \underset{\sim}{q}_m)$$

$$\times \left(\frac{\hbar^m}{2^m \omega_{\underset{\sim}{q}_1 j_1} \cdots \omega_{\underset{\sim}{q}_m j_m}} \right)^{1/2} \Phi(\underset{\sim}{q}_1 j_1 \cdots \underset{\sim}{q}_m j_m) \tag{5.7}$$

where

$$\Phi(\underset{\sim}{q}_1 j_1 \cdots \underset{\sim}{q}_m j_m)$$

$$= \frac{1}{2M^{m/2}} \sum_n{}' \sum_{\alpha_1 \cdots \alpha_m} e_{\alpha_1}(\underset{\sim}{q}_1 j_1) \cdots e_{\alpha_m}(\underset{\sim}{q}_m j_m)$$

$$\times \phi_{\alpha_1 \cdots \alpha_m}(|\underset{\sim}{r}_n|)(1 - e^{-i\underset{\sim}{q}_1 \cdot \underset{\sim}{r}_n}) \cdots (1 - e^{-i\underset{\sim}{q}_m \cdot \underset{\sim}{r}_n}) \tag{5.8}$$

and $\phi_{\alpha_1 \cdots \alpha_m}(|\underset{\sim}{r}_n|)$ is the m th order tensor derivative of a two-body potential $\Phi(|\underset{\sim}{r}_n|)$ with $\alpha_1 \cdots \alpha_m$ each running over the Cartesian indices x, y, z; $\underset{\sim}{r}_n = \frac{a}{2}(n_x, n_y, n_z)$ and for a b.c.c. lattice n_x, n_y, n_z are either all odd or all even integers. M and N denote the atomic mass and number of unit cells in the crystal. The prime in Eq. (5.8) denotes the omission of the origin point $\underset{\sim}{r}_n = (0.0.0)$

5.4 THE QUARTIC SHIFT (QS) CONTRIBUTION TO THE PHONON-LIMITED RESISTIVITY OF METALS (ρ)

The calculation of QS naturally requires the knowledge of the Fourier transform of the anharmonic force constant. $V^4(\underset{\sim}{q}_1 j_1, -\underset{\sim}{q}_1 j_1, \underset{\sim}{q}j, -\underset{\sim}{q}j)$. Using Eqs. (5.7) and (5.8), we can write the expression for the QS given by Eq. (4.5) as follows:

$$\Delta^4_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) = \frac{24}{\beta\hbar^2}\left(\frac{4\hbar^2}{24N\cdot 4\cdot 2M^2}\right)\sum_n{}' \sum_{\underset{\sim}{q}_1 j_1}\sum_{\alpha\beta\gamma\delta}\phi_{\alpha\beta\gamma\delta}(|\underset{\sim}{r}_n|)$$

$$\times \frac{e_\alpha(\underset{\sim}{q}_1 j_1)\, e_\beta(-\underset{\sim}{q}_1 j_1)\, e_\gamma(\underset{\sim}{q}j)\, e_\delta(-\underset{\sim}{q}j)}{\omega^2_{\underset{\sim}{q}_1 j_1}\,\omega_{\underset{\sim}{q}j}}$$

$$\times (1-\cos(\underset{\sim}{q}_1\cdot\underset{\sim}{r}_n))(1-\cos(\underset{\sim}{q}\cdot\underset{\sim}{r}_n)) \qquad (5.9)$$

Combining the two cosine terms in Eq. (5.9) and defining the fourth rank tensor sum for a wave vector $\underset{\sim}{Q}$ as

$$F_{\alpha\beta\gamma\delta}(\underset{\sim}{Q}) = \sum_n{}' \phi_{\alpha\beta\gamma\delta}(|\underset{\sim}{r}_n|)\cos(\underset{\sim}{Q}\cdot\underset{\sim}{r}_n) \qquad (5.10)$$

we can express Eq. (5.9) in terms of $F_{\alpha\beta\gamma\delta}(\underset{\sim}{Q})$, i.e.,

$$\Delta^4_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) = \frac{1}{\beta}\left(\frac{1}{2NM^2}\right)\sum_{\underset{\sim}{q}_1 j_1}\sum_{\alpha\beta\gamma\delta}\frac{e_\alpha(\underset{\sim}{q}_1 j_1)\, e_\beta(-\underset{\sim}{q}_1 j_1)}{\omega^2_{\underset{\sim}{q}_1 j_1}}$$

$$\times \frac{e_\gamma(\underset{\sim}{q}j)\, e_\delta(-\underset{\sim}{q}j)}{\omega_{\underset{\sim}{q}j}}\Big[F_{\alpha\beta\gamma\delta}(\underset{\sim}{0}) - F_{\alpha\beta\gamma\delta}(\underset{\sim}{q})$$

$$- F_{\alpha\beta\gamma\delta}(\underset{\sim}{q}_1) + \frac{1}{2}F_{\alpha\beta\gamma\delta}(\underset{\sim}{q}+\underset{\sim}{q}_1) + \frac{1}{2}F_{\alpha\beta\gamma\delta}(\underset{\sim}{q}-\underset{\sim}{q}_1)\Big] \qquad (5.11)$$

Since $\underset{\sim}{q}_1$ takes all possible values in the summation, changing $\underset{\sim}{q}_1$ to $-\underset{\sim}{q}_1$, the last two terms are equivalent, and finally Eq. (5.11) can be written as:

$$\Delta^4_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) = \left[\Delta^4_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j})\right]_1 - \left[\Delta^4_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j})\right]_2 - \left[\Delta^4_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j})\right]_3 + \left[\Delta^4_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j})\right]_4 \tag{5.12}$$

where

$$\left[\Delta^4_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j})\right]_\ell = \frac{1}{2\beta MN^2} \sum_{\alpha\beta\gamma\delta} \frac{e_\gamma(\underset{\sim}{q}j)\, e_\delta(-\underset{\sim}{q}j)}{\omega_{\underset{\sim}{q}j}} \left[Z_{\alpha\beta\gamma\delta}\right]_\ell \tag{5.12a}$$

and in particular

$$\left[Z_{\alpha\beta\gamma\delta}\right]_1 = F_{\alpha\beta\gamma\delta}(\underset{\sim}{0})\, S_{\alpha\beta}(0) \tag{5.12b}$$

$$\left[Z_{\alpha\beta\gamma\delta}\right]_2 = F_{\alpha\beta\gamma\delta}(\underset{\sim}{q})\, S_{\alpha\beta}(0) \tag{5.12c}$$

$$\left[Z_{\alpha\beta\gamma\delta}\right]_3 = S_{\alpha\beta\gamma\delta}(\underset{\sim}{0}, 0) \tag{5.12e}$$

$$\left[Z_{\alpha\beta\gamma\delta}\right]_4 = S_{\alpha\beta\gamma\delta}(\underset{\sim}{q}, 0) \tag{5.12f}$$

where

$$S_{\alpha\beta\gamma\delta}(\underset{\sim}{q}, \ell) = \sum_{\underset{\sim}{q}_1 j_1} \frac{e_\alpha(\underset{\sim}{q}_1 j_1)\, e_\beta(\underset{\sim}{q}_1 j_1)}{\omega^2_{\underset{\sim}{q}_1 j_1}} F_{\alpha\beta\gamma\delta}(\underset{\sim}{q}_1 + \underset{\sim}{q}) \cos(\underset{\sim}{q}_1 \cdot \underset{\sim}{r}_\ell) \tag{5.13}$$

and the B.Z. sum $S_{\alpha\beta}(n)$ is defined by Eq. (5.3).

The calculation of the whole B.Z. sum $S_{\alpha\beta}(n)$ can be reduced to that of the Ir. F.B.Z. (as shown by Shukla and Wilk (1974)) but this is not possible for the function $S_{\alpha\beta\gamma\delta}(\underset{\sim}{q},\ell)$, because of the $\underset{\sim}{q}$ and $\underset{\sim}{q}_1$ dependence of the part of the summand $F_{\alpha\beta\gamma\delta}$ in Eq. (5.13). However, the reduction can be achieved by introducing the Δ function $\Delta(\underset{\sim}{q} + \underset{\sim}{q}_1 - \underset{\sim}{Q})$ in Eq. (5.13). Using the plane wave representation of the Δ function, Eq. (5.5), rearranging the terms and introducing the function $G_{\alpha\beta\gamma\delta}(n)$, defined below, we can write Eq. (5.13) for $\ell = 0$ in the following form:

$$S_{\alpha\beta\gamma\delta}(\underset{\sim}{q},0) = \frac{1}{N}\sum_{n}\cos(\underset{\sim}{q}\cdot\underset{\sim}{r}_n)\, S_{\alpha\beta}(n)\sum_{\underset{\sim}{Q}} F_{\alpha\beta\gamma\delta}(\underset{\sim}{Q})\cos(\underset{\sim}{Q}\cdot\underset{\sim}{r}_n)$$

$$= \frac{1}{N}\sum_{n}\cos(\underset{\sim}{q}\cdot\underset{\sim}{r}_n)\, S_{\alpha\beta}(n)\, G_{\alpha\beta\gamma\delta}(n) \qquad (5.14)$$

where

$$G_{\alpha\beta\gamma\delta}(n) = \sum_{\underset{\sim}{Q}} F_{\alpha\beta\gamma\delta}(\underset{\sim}{Q})\cos(\underset{\sim}{Q}\cdot\underset{\sim}{r}_n) \qquad (5.15)$$

Now the B.Z. sum represented by $G_{\alpha\beta\gamma\delta}(n)$ can be calculated in the Ir.F.B.Z. by the method given in Shukla and Wilk (1974). The second and fourth rank tensors in Eq. (5.14) can be combined to give one fourth rank tensor. Thus the sum in $S_{\alpha\beta\gamma\delta}(\underset{\sim}{q},n)$, Eq. (5.14) can be easily carried out for a n th lattice point in the s th shell having n^s lattice points following essentially the same procedure as has been suggested by Shukla and Wilk (1974) for a reciprocal space summation. In fact the invariant form of expressions in n and q spaces are exactly similar and only the cartesian components of $\underset{\sim}{R}_n$ and $\underset{\sim}{q}$ are interchanged.

We have computed the fourth rank tensor sum, Eq. (5.10), accurately to nine significant figures for a given wave vector $\underset{\sim}{q}$ by the Ewald procedure (1921). The B.Z. sum $G_{\alpha\beta\gamma\delta}(n)$ is computed to an accuracy of three significant digits for L = 52, i.e., a mesh size of 910 wave vector in the Ir.F.B.Z. In order to compute the function $S_{\alpha\beta\gamma\delta}(\underset{\sim}{q},0)$ accurately to seven figures, for a given $\underset{\sim}{q}$, it is necessary to carry out the direct lattice n sum, arising in Eq. (5.14), up to the 23 rd shell.

Once the tensor sums described above have been computed, the numerical calculation of the QS $\Delta^{4}_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j})$ as given by Eq. (5.12) is straight forward. The integrand in Eq. (4.4) is then easily computed with the help of the QS $\Delta^{4}_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j})$ and the integral is evaluated exactly in the same manner as described in Section 5. The numerical results of these calculations which represent the QS contribution to ρ for Na and K are presented in Tables 3 and 6 respectively.

5.5 THE CUBIC SHIFT (CS) CONTRIBUTION TO THE PHONON-LIMITED RESISTIVITY OF METALS (ρ)

Substituting for $V^3(-\underset{\sim}{q}j, \underset{\sim}{q}_1 j_1, \underset{\sim}{q}_2 j_2)$ as obtained from the general Eqs. (5.7) and (5.8) into Eq. (4.3), performing the sums over the direct lattice vectors ($\underset{\sim}{r}_n$) first and defining the third rank tensor sum for a fixed wave vector $\underset{\sim}{Q}$ (Shukla and Taylor (1974))

$$F_{\alpha\beta\gamma}(\underset{\sim}{Q}) = \sum_n{}' \Phi_{\alpha\beta\gamma}(|\underset{\sim}{r}_n|) \sin(\underset{\sim}{Q}\cdot\underset{\sim}{r}_n) \tag{5.16}$$

we can write Eq. (4.3) as

$$\Delta^3_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) = \frac{1}{2^3\beta M^3 N} \sum_{\substack{q_1 q_2 \\ j_1 j_2}} \frac{\Delta(-\underset{\sim}{q}+\underset{\sim}{q}_1+\underset{\sim}{q}_2)}{\omega_{\underset{\sim}{q}j}\,\omega_{\underset{\sim}{q}_1 j_1}\,\omega_{\underset{\sim}{q}_2 j_2}}$$

$$\times \sum_{\alpha\beta\gamma\lambda\mu\nu} e_\alpha(-\underset{\sim}{q}j)\, e_\lambda(-\underset{\sim}{q}j)\, e_\beta(\underset{\sim}{q}_1 j_1)\, e_\mu(\underset{\sim}{q}_1 j_1)\, e_\gamma(\underset{\sim}{q}_2 j_2)\, e_\nu(\underset{\sim}{q}_2 j_2)$$

$$\times \left[-F_{\alpha\beta\gamma}(\underset{\sim}{q}) + F_{\alpha\beta\gamma}(\underset{\sim}{q}_1) + F_{\alpha\beta\gamma}(\underset{\sim}{q}_2)\right]\left[-F_{\lambda\mu\nu}(\underset{\sim}{q}) + F_{\lambda\mu\nu}(\underset{\sim}{q}_1) + F_{\lambda\mu\nu}(\underset{\sim}{q}_2)\right]$$

$$\times \frac{1}{\omega_{\underset{\sim}{q}_1 j_1}\,\omega_{\underset{\sim}{q}_2 j_2}}\, P\left[\frac{(\omega_{\underset{\sim}{q}_1 j_1}+\omega_{\underset{\sim}{q}_2 j_2})^2}{\omega_{\underset{\sim}{q}j}^2-(\omega_{\underset{\sim}{q}_1 j_1}+\omega_{\underset{\sim}{q}_2 j_2})^2} - \frac{(\omega_{\underset{\sim}{q}_1 j_1}-\omega_{\underset{\sim}{q}_2 j_2})^2}{\omega_{\underset{\sim}{q}j}^2-(\omega_{\underset{\sim}{q}_1 j_1}-\omega_{\underset{\sim}{q}_2 j_2})^2}\right] \tag{5.17}$$

On comparing the summands arising in $\Delta^3_{qj}(\omega_{qj})$, Eq. (5.17) and $M(\underset{\sim}{q})$, (Eq. (4.13)), we notice the same complication in the calculation, i.e., the double sum $\underset{\sim}{q}_1$ and $\underset{\sim}{q}_2$ over the B.Z. and the restriction on the wave vectors through the Δ function $\Delta(-\underset{\sim}{q} + \underset{\sim}{q}_1 + \underset{\sim}{q}_2)$. We also have the added difficulty in Eq. (5.17) of the evaluation of the principle part and several multiple summations over the indices α, β, γ, λ, μ, ν

arising in the tensors $F_{\alpha\beta\gamma}(\underset{\sim}{Q})$, $F_{\lambda\mu\nu}(\underset{\sim}{Q})$, and the eigenvectors $\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}$. Unfortunately the Δ function in Eq. (5.17) cannot be replaced by a plane wave sum over the direct lattice vectors as was done in Section 5.2 and the numerical evaluation of Eq. (5.17) requires the testing of this function. All this is extremely time consuming and cumbersome.

Fortunately, the CS of the phonon frequencies ($\omega_{\underset{\sim}{q}j}$) (Eq. (5.17)) for a few selected wave vectors, have been calculated by Glyde and Taylor (1971). In their calculations of the CS they used the self-consistent phonon theory to obtain the frequencies $\omega_{\underset{\sim}{q}j}$ and eigenvectors $\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}$ and $\phi_{\alpha\beta\gamma}$ was replaced by the average $\langle\phi_{\alpha\beta\gamma}\rangle$. These shifts are presented here in Table 15. For the sake of comparison we also present in Table 15 our values of the QS for the same wave vectors. From Table 15 we see that the two shifts are almost of the same order of magnitude but opposite in sign. Although this comparison is shown here for selected wave vectors only, there is no reason to believe that this correspondence would not be true for "all" wave vectors.

Since the two shifts are just about of the same order of magnitude but opposite in sign, the contribution to ρ from them would also be of the same order of magnitude but opposite in sign.

Therefore if the contribution to ρ from the QS as given by Eqs. (4.4) and (4.5), is computed exactly, there would be little point in computing the contribution to ρ from the CS, Eqs. (4.2) and (4.3), separately. Since the exact calculation of the CS, Eq. (5.17), can consume hours of computing time, we decided to compute the contribution to ρ exactly from the QS as the contribution to ρ from the CS is then more or less also known from the above comparison of the two shifts.

However, since the contributions to ρ from the QS and CS do not have complete cancellation, we would like to get some idea of the extent of cancellation without spending excessive computer time. This can be done by the calculation of the contributions to ρ from the QS and CS in the partial Einstein approximation (PEA) or the total Einstein approximation (TEA).

The Total and Partial Einstein Approximations

The simplest way to introduce these approximations in the context of the calculation of ρ is as follows. Consider for example a typical function, f, of $\omega_{\underset{\sim}{q}j}$ and $\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}$ arising in Eqs. (5.1) and (5.2):

$$f(\omega_{\underset{\sim}{q}j}, \underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}) = g(\omega_{\underset{\sim}{q}j}, \underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}) \sum_{\underset{\sim}{q}_1 j_1} h(\omega_{\underset{\sim}{q}j}, \underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}, \omega_{\underset{\sim}{q}_1 j_1}, \underset{\sim}{\varepsilon}_{\underset{\sim}{q}_1 j_1}) \tag{5.18}$$

If in Eq. (5.18), the summation over $\underset{\sim}{q}_1 j_1$ for a fixed $\underset{\sim}{q}j$ is performed under the assumption that for all $\underset{\sim}{q}_1 j_1$, $\omega_{\underset{\sim}{q}_1 j_1} = \omega_E$, the Einstein frequency, then $f(\omega_{\underset{\sim}{q}j}, \underset{\sim}{\varepsilon}_{\underset{\sim}{q}j})$ is evaluated in the PEA and the integral in Eqs. (5.1) and (5.2) is done exactly, i.e., $\omega_{\underset{\sim}{q}j} \neq \omega_E$. Here, ω_E is obtained by

$$\omega_E = \left(\sum_{\underset{\sim}{q}_1 j_1}^{B.Z.} \omega^2_{\underset{\sim}{q}_1 j_1} \Big/ \sum_{\underset{\sim}{q}_1 j_1}^{B.Z.} 1 \right)^{1/2} \tag{5.19}$$

In the total Einstein approximation in evaluating Eq. (5.18), not only are all $\omega_{\underset{\sim}{q}_1 j_1}$ set equal to ω_E, but $\omega_{\underset{\sim}{q}j}$ is also set equal to ω_E'. Here ω_E' is obtained by

$$\omega_E' = \left(\sum_{\substack{qj \\ |q|<2k_F}} \omega_{qj}^2 \Big/ \sum_{\substack{qj \\ |q|<2k_F}} 1 \right)^{1/2} \tag{5.20}$$

The Calculation of $\Delta^3_{qj}(\omega_{qj})$ in the Total and Partial Einstein Approximation

In the PEA of $\Delta^3_{qj}(\omega_{qj})$, we set $\omega_{q_1j_1} = \omega_{q_2j_2} = \omega_E$ and using the orthonormal properties of ε_{qj}, Eq. (5.17) reduces to

$$\Delta^3_{qj}(\omega_{qj}) = \frac{-1}{2^3\beta M^3 N} \sum_{q_1 q_2} \frac{\Delta(-q+q_1+q_2)}{\omega_{qj}\,\omega_E^2}$$

$$\times \sum_{\alpha\beta\gamma\lambda} e_\alpha(-qj)\, e_\lambda(-qj) \left[-F_{\alpha\beta\gamma}(q) + F_{\alpha\beta\gamma}(q_1) + F_{\alpha\beta\gamma}(q_2) \right]$$

$$\times \left[-F_{\lambda\beta\gamma}(q) + F_{\lambda\beta\gamma}(q_1) + F_{\lambda\beta\gamma}(q_2) \right] P \left[\frac{4}{\omega_{qj}^2 - 4\omega_E^2} \right] \tag{5.21}$$

At this stage it is possible to substitute the plane wave representation of the Δ function as defined by Eq. (5.5) in Eq. (5.21). Introducing this representation and employing the fact that

$$\sum_{Q} e^{iQ\cdot r_n} = N\Delta(r_n) \tag{5.22}$$

we obtain after multiplication of the terms in square brackets and some rearrangement, the expression

$$\Delta^{3}_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) = \frac{1}{2^3\beta M^3 N} P\left[\frac{4}{\omega_{\underset{\sim}{q}j}^2 - \omega_E^2}\right]\frac{1}{\omega_{\underset{\sim}{q}j}\omega_E^2}\sum_n \sum_{\alpha\beta\gamma\lambda} e_\alpha(-\underset{\sim}{q}j)\, e_\lambda(-\underset{\sim}{q}j)$$

$$\times\Big\{N^2 F_{\alpha\beta\gamma}(\underset{\sim}{q}) F_{\lambda\beta\gamma}(\underset{\sim}{q}) - N F_{\alpha\beta\gamma}(\underset{\sim}{q})\sum_{\underset{\sim}{q}_1} F_{\lambda\beta\gamma}(\underset{\sim}{q}_1)$$

$$- N F_{\alpha\beta\gamma}(\underset{\sim}{q})\sum_{\underset{\sim}{q}_2} F_{\lambda\beta\gamma}(\underset{\sim}{q}_2) - N F_{\lambda\beta\gamma}(\underset{\sim}{q})\sum_{\underset{\sim}{q}_1} F_{\alpha\beta\gamma}(\underset{\sim}{q}_1)$$

$$- N F_{\lambda\beta\gamma}(\underset{\sim}{q})\sum_{\underset{\sim}{q}_2} F_{\alpha\beta\gamma}(\underset{\sim}{q}_2) + N\sum_{\underset{\sim}{q}_1} F_{\alpha\beta\gamma}(\underset{\sim}{q}_1) F_{\lambda\beta\gamma}(\underset{\sim}{q}_1)$$

$$+ N\sum_{\underset{\sim}{q}_2} F_{\alpha\beta\gamma}(\underset{\sim}{q}_2) F_{\lambda\beta\gamma}(\underset{\sim}{q}_2) + \sum_n e^{-i\underset{\sim}{q}\cdot\underset{\sim}{r}_n}\sum_{\underset{\sim}{q}_1} F_{\alpha\beta\gamma}(\underset{\sim}{q}_1)\, e^{i\underset{\sim}{q}_1\cdot\underset{\sim}{r}_n}$$

$$\times\sum_{\underset{\sim}{q}_2} F_{\lambda\beta\gamma}(\underset{\sim}{q}_2)\, e^{i\underset{\sim}{q}_2\cdot\underset{\sim}{r}_n} + \sum_n e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_n}\sum_{\underset{\sim}{q}_1} F_{\lambda\beta\gamma}(\underset{\sim}{q}_1)\, e^{i\underset{\sim}{q}_1\cdot\underset{\sim}{r}_n}$$

$$\times\sum_{\underset{\sim}{q}_2} F_{\alpha\beta\gamma}(\underset{\sim}{q}_2)\, e^{i\underset{\sim}{q}_2\cdot\underset{\sim}{r}_n}\Big\} \tag{5.23}$$

We see that the expression given by Eq. (5.21) contains the B.Z. sums of the type

$$G_{\alpha\beta\gamma} = \sum_{\underset{\sim}{Q}} F_{\alpha\beta\gamma}(\underset{\sim}{Q}) \tag{5.24}$$

Substituting for the third rank tensor $F_{\alpha\beta\gamma}(\underset{\sim}{Q})$ given by Eq. (5.16) in Eq. (5.24), we obtain the following:

$$G_{\alpha\beta\gamma} = \sum_{\underset{\sim}{Q}} \sum_{n}{}' \phi_{\alpha\beta\gamma}(|\underset{\sim}{r}_n|) \sin(\underset{\sim}{Q}\cdot\underset{\sim}{r}_n)$$

$$= \frac{1}{2i} \sum_{n}{}' \phi_{\alpha\beta\gamma}(|\underset{\sim}{r}_n|) \sum_{\underset{\sim}{Q}} \left\{ e^{i\underset{\sim}{Q}\cdot\underset{\sim}{r}_n} - e^{-i\underset{\sim}{Q}\cdot\underset{\sim}{r}_n} \right\} \tag{5.25}$$

Employing Eq. (5.22) in Eq. (5.25) we obtain the following result:

$$G_{\alpha\beta\gamma} = \frac{N}{2i} \sum_{n}{}' \phi_{\alpha\beta\gamma}(|\underset{\sim}{r}_n|) \left[\Delta(\underset{\sim}{r}_n) - \Delta(-\underset{\sim}{r}_n)\right]$$

$$= 0 \tag{5.26}$$

Since $\Delta(\underset{\sim}{r}_n) = 0$ for $\underset{\sim}{r}_n \neq (0.0.0)$. Employing the result of Eq. (5.26) in Eq. (5.23) and noting that

$$\sum_{\underset{\sim}{q}_1} F_{\alpha\beta\gamma}(\underset{\sim}{q}_1)\, F_{\lambda\beta\gamma}(\underset{\sim}{q}_1) = \sum_{\underset{\sim}{q}_2} F_{\alpha\beta\gamma}(\underset{\sim}{q}_2)\, F_{\lambda\beta\gamma}(\underset{\sim}{q}_2)$$

we can reduce Eq. (5.23) to the following form:

$$\Delta^3_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) = \left[\Delta^3_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j})\right]_1 + \left[\Delta^3_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j})\right]_2 + \left[\Delta^3_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j})\right]_3 \tag{5.27}$$

where

$$\left[\Delta^3_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j})\right]_\ell = A \sum_{\alpha\beta\gamma\lambda} e_\alpha(-\underset{\sim}{q}j)\, e_\lambda(-\underset{\sim}{q}j) \left[H_{\alpha\beta\gamma\lambda}\right]_\ell \quad \text{for } \ell = 1,2,3 \tag{5.28}$$

In particular A and $[H_{\alpha\beta\gamma\lambda}]_\ell$ are given by

$$A = \frac{1}{2^3 \beta M^3 N} \left(\frac{1}{\omega_{\underset{\sim}{q}j}\, \omega_E^2}\right) P \left[\frac{4}{\omega^2_{\underset{\sim}{q}j} - \omega_E^2}\right]$$

$$\left[H_{\alpha\beta\gamma\lambda}\right]_1 = N^2 F_{\alpha\beta\gamma}(\underset{\sim}{q}) F_{\lambda\beta\gamma}(\underset{\sim}{q}) \tag{5.29}$$

$$\left[H_{\alpha\beta\gamma\lambda}\right]_2 = 2N \sum_{\underset{\sim}{q}_1} F_{\alpha\beta\gamma}(\underset{\sim}{q}_1) F_{\lambda\beta\gamma}(\underset{\sim}{q}_1) \tag{5.30}$$

$$\left[H_{\alpha\beta\gamma\lambda}\right]_3 = \frac{2}{N} \sum_{n} \cos(\underset{\sim}{q}\cdot\underset{\sim}{r}_n)\, G_{\alpha\beta\gamma}(n)\, G_{\lambda\beta\gamma}(n) \tag{5.31}$$

where

$$G_{\alpha\beta\gamma}(n) = \sum_{\underset{\sim}{Q}} F_{\alpha\beta\gamma}(\underset{\sim}{Q}) \sin(\underset{\sim}{Q}\cdot\underset{\sim}{r}_n) \tag{5.32}$$

The calculation of the B.Z. sum $G_{\alpha\beta\gamma}(n)$, given by Eq. (5.32), can be reduced to that of the Ir. F.B.Z. by the method described by Shukla and Taylor (1974) for a real space summation. Even though we have a B.Z. summation in Eq. (5.32), the invariant form is exactly similar except for the interchange of the components of the vectors $\underset{\sim}{r}_n$ and $\underset{\sim}{q}$. Also the tensor $[H_{\alpha\beta\gamma\lambda}]$ (ℓ = 1, 2, 3) can be computed in a similar manner as the tensor $S_{\alpha\beta\gamma\delta}(\underset{\sim}{q},\ell)$ defined by Eq. (5.13).

Generating the wave vectors $\underset{\sim}{q}_1$ in the Ir. F.B.Z. and obtaining the corresponding eigenvalues $\omega_{\underset{\sim}{q}_1 j_1}$, described in Section 5, we can obtain ω_E and ω_E' from Eqs. (5.19) and (5.20) respectively. To obtain ω_E and ω_E' to an accuracy of seven significant figures, we have used the step length (L = 20). The Einstein frequencies ω_E and ω_E' obtained for Na and K are presented in Table 16.

Once the above tensors and the Einstein frequencies have been computed, the numerical calculation of the cubic shift (CS) as defined by Eq. (5.27) is straightforward. The numerical values for CS for different $\underset{\sim}{q}$ vectors are then employed in the integrand of Eq. (4.2) and the evaluation of the integral is carried out as described previously in Section 5.

When the above calculation is carried out in the total Einstein approximation, the only change occurs in the constant A, which is now given by:

$$A = \frac{1}{2^3 \beta M^3 N} \left(\frac{1}{\omega_E' \omega_E^2} \right) P \left[\frac{4}{\omega_E'^2 - 4\omega_E^2} \right]$$

The numerical results for Na and K for the CS contribution to ρ calculated in the partial and total Einstein approximations are presented in Tables 4 and 7, respectively.

5.6 THE QUARTIC SHIFT (QS) CONTRIBUTION TO THE PHONON-LIMITED RESISITIVITY OF METALS (ρ) IN THE PARTIAL AND TOTAL EINSTEIN APPROXIMATION

Although we have performed the exact calculation of the quartic shift contribution to ρ (see Sec. 5.3), we present the calculation again in the partial and total Einstein approximation because the cubic shift contribution to ρ in these approximations has been computed previously (see Sec. 5.5). Hopefully, this will provide a much better idea of the extent of cancellation between the contributions to ρ from the cubic and quartic shift.

In the Einstein approximation, the B.Z. sums $S_{\alpha\beta}(n)$ and $S_{\alpha\beta\gamma\delta}(\underset{\sim}{q},n)$ as given by Eqs. (5.3) and (5.13) respectively, reduce to the following form:

$$S_{\alpha\beta}(n) = \frac{1}{\omega_E^2} \sum_{\underset{\sim}{q}_1} \delta_{\alpha\beta} \cos(\underset{\sim}{q}_1 \cdot \underset{\sim}{r}_n) \tag{5.33}$$

$$S_{\alpha\beta\gamma\delta}(\underset{\sim}{q},n) = \frac{1}{\omega_E^2} \sum_{\underset{\sim}{q}_1} F_{\alpha\beta\gamma\delta}(\underset{\sim}{q}_1 + \underset{\sim}{q})\, \delta_{\alpha\beta} \cos(\underset{\sim}{q}_1 \cdot \underset{\sim}{r}_n) \tag{5.34}$$

where in obtaining Eqs. (5.33) and (5.34) we have set $\omega_{\underset{\sim}{q}j} = \omega_E$ and used the orthonormal property of the eigenvectors ($\hat{\varepsilon}_{\underset{\sim}{q}j}$) in Eqs. (5.3) and (5.13). Substituting Eqs. (5.33) and (5.34) into Eq. (5.12), we obtain the following expression for the QS in PEA.

$$\Delta^4_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) = \frac{1}{2\beta M N^2} \sum_{\alpha\gamma\delta} \frac{e_\alpha(\underset{\sim}{q}j)\, e_\beta(\underset{\sim}{q}j)}{\omega_{\underset{\sim}{q}j}\, \omega_E^2}$$

$$\times \Big[F_{\alpha\alpha\gamma\delta}(\underset{\sim}{0}) - F_{\alpha\alpha\gamma\delta}(\underset{\sim}{q}) - \sum_{\underset{\sim}{q}_1} F_{\alpha\alpha\gamma\delta}(\underset{\sim}{q}_1)$$

$$+ \sum_{\underset{\sim}{q}_1} F_{\alpha\alpha\gamma\delta}(\underset{\sim}{q} + \underset{\sim}{q}_1) \Big] \tag{5.35}$$

Since $\langle \underset{\sim}{q}_1 + \underset{\sim}{q} \rangle$ set differs from the $\langle \underset{\sim}{q}_1 \rangle$ by a vector of the reciprocal lattice ($\underset{\sim}{\tau}$) and $F_{\alpha\beta\gamma\delta}(\underset{\sim}{q}_1 + \underset{\sim}{\tau}) = F_{\alpha\beta\gamma\delta}(\underset{\sim}{q}_1)$ due to the periodicity of the function $F_{\alpha\beta\gamma\delta}(\underset{\sim}{q})$, we find that the last two terms in Eq. (5.35) cancel each other. Thus we are left with

$$\Delta^4_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) = \frac{1}{2\beta MN^2} \sum_{\alpha\gamma\delta} \frac{e_\gamma(\underset{\sim}{q}j)\, e_\delta(-\underset{\sim}{q}j)}{\omega_{\underset{\sim}{q}j}\, \omega_E^2} \left[F_{\alpha\alpha\gamma\delta}(\underset{\sim}{0}) - F_{\alpha\alpha\gamma\delta}(\underset{\sim}{q}) \right] \tag{5.36}$$

Since the R.H.S. in Eq. (5.36) is independent of any Brillouin zone sum, this expression can be employed to obtain exact values of the QS in the partial Einstein approximation as well as check the correctness of our computer program. This is done by setting $\omega_{\underset{\sim}{q}_1 j_1} = \omega_E$ in the $\underset{\sim}{q}_1 j_1$ loop of the computer program and checking if this big computer program produces the same values as obtained from Eq. (5.36).

The numerical values of the QS, given by Eq. (5.36), for different $\underset{\sim}{q}$ are then employed in Eq. (4.4), which is evaluated exactly in the same manner as described in Section 5. The numerical results for the QS contribution to ρ for Na and K in the PEA are presented in Tables 4 and 7 respectively. In the TEA, the QS, as given by Eq. (5.36), becomes

$$\Delta^4_{\underset{\sim}{q}j}(\omega_E') = \frac{1}{2\beta MN^2} \sum_{\alpha\beta\gamma} \frac{e_\gamma(\underset{\sim}{q}j)\, e_\delta(-\underset{\sim}{q}j)}{\omega_E'\, \omega_E^2} \left[F_{\alpha\alpha\gamma\delta}(\underset{\sim}{0}) - F_{\alpha\alpha\gamma\delta}(\underset{\sim}{q}) \right] \tag{5.37}$$

The numerical results obtained from Eq. (5.37) are incorporated in the numerical calculation of Eq. (4.4) and the contribution to ρ for Na and K from the QS in the TEA are presented in Tables 4 and 7, respectively.

5.7 THE WIDTH (W) CONTRIBUTION TO THE PHONON-LIMITED RESISTIVITY OF METALS (ρ) IN THE PARTIAL AND TOTAL EINSTEIN APPROXIMATION

Since the structure of the CS (Eq. (4.3)) and the W (Eq. (4.7)) are so similar, we decided to do the calculation of the W also in the Einstein approximation. Using the same procedure as that used in the CS calculation, we obtain the following expression for the W (Eq. (4.7)) in the PEA:

$$W_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) = \left[W_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j})\right]_1 + \left[W_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j})\right]_2 + \left[W_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j})\right]_3 \qquad (5.38)$$

where

$$\left[W_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j})\right]_\ell = B \sum_{\alpha\beta\gamma\lambda} e_\alpha(-\underset{\sim}{q}j)\, e_\beta(-\underset{\sim}{q}j) \left[H_{\alpha\beta\gamma\lambda}\right]_\ell \qquad (5.39)$$

and in particular

$$B = \frac{1}{2^3 \beta M^3 N}\left(\frac{1}{\omega_{\underset{\sim}{q}j}\,\omega_E^2}\right)\left[\frac{1}{\omega_E^2(\omega_{\underset{\sim}{q}j} - 2\omega_E)^2} + \frac{1}{\omega_E^2\,\omega_{\underset{\sim}{q}j}^2}\right]$$

and $[H_{\alpha\beta\gamma\lambda}]_\ell$ is defined by Eqs. (5.29), (5.30) and (5.31).

We have computed the phonon width as given by Eq. (5.38) in the same manner as described in Section 5.4 for the CS. The numerical results for the phonon width are then employed in Eq. (4.6) which is evaluated exactly in the same manner as described in Section 5. The results for the W contribution to ρ in the PEA for Na and K are presented in Tables 9 and 11, respectively. In the case of the TEA the only change in the expression for the W, given by Eqs. (5.38) and (5.39) is that the constant B in Eq. (5.39) becomes:

$$B = \frac{1}{2^3 \beta M^3 N} \left(\frac{1}{\omega_E' \omega_E^2} \right) \left[\frac{1}{\omega_E^2 (\omega_E' - 2\omega_E)^2} + \frac{1}{\omega_E^2 \omega_E'^2} \right]$$

The results for the W contribution to ρ for Na and K in the TEA are presented in Tables 10 and 12, respectively.

5.8 THE INTERFERENCE (I) TERM CONTRIBUTION TO THE PHONON-LIMITED RESISTIVITY OF METALS (ρ) IN THE PARTIAL AND TOTAL EINSTEIN APPROXIMATION

The high temperature limit expression for the interference term contribution to ρ involves the Fourier transform $V^3(-\underset{\sim}{q}_1 j_1, -\underset{\sim}{q}_2 j_2, \underset{\sim}{q} j)$. Substituting for $V^3(-\underset{\sim}{q}_1 j_1, -\underset{\sim}{q}_2 j_2, \underset{\sim}{q} j)$ from Eqs. (5.7), (5.8) into Eq. (4.9) and expanding the dot products arising in Eq. (4.9), we obtain

$$I_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) = \frac{-i\,2^{3/2}}{3\hbar^{3/2}\beta^{3}N^{1/2}M^{3/2}} \sum_{\substack{q_1 q_2 \\ j_1 j_2}} \frac{\Delta(-\underset{\sim}{q}+\underset{\sim}{q}_1+\underset{\sim}{q}_2)}{(\omega_{\underset{\sim}{q}_1 j_1}\,\omega_{\underset{\sim}{q}_2 j_2}\,\omega_{\underset{\sim}{q}j})^2}$$

$$\times \sum_{\alpha\beta\gamma\lambda\mu\nu} q_\alpha q_\beta q_\gamma\, e_\alpha(-\underset{\sim}{q}j)\, e_\nu(\underset{\sim}{q}j)\, e_\beta(\underset{\sim}{q}_1 j_1)\, e_\lambda(-\underset{\sim}{q}_1 j_1)$$

$$\times\, e_\gamma(\underset{\sim}{q}_2 j_2)\, e_\lambda(\underset{\sim}{q}_2 j_2) \left[F_{\lambda\mu\nu}(\underset{\sim}{q}) - F_{\lambda\mu\nu}(\underset{\sim}{q}_1) - F_{\lambda\mu\nu}(\underset{\sim}{q}_2)\right] \qquad (5.40)$$

Here in applying the partial Einstein approximation, we set $\omega_{\underset{\sim}{q}_1 j_1} = \omega_{\underset{\sim}{q}_2 j_2}$ for all values of $\underset{\sim}{q}_1 j_1$ and $\underset{\sim}{q}_2 j_2$ in the double sum arising in Eq. (5.40). This yields

$$I_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) = \frac{-i\,2^{3/2}}{3\hbar^{3/2}\beta^{3}N^{1/2}M^{3/2}} \sum_{\underset{\sim}{q}_1 \underset{\sim}{q}_2} \frac{\Delta(-\underset{\sim}{q}+\underset{\sim}{q}_1+\underset{\sim}{q}_2)}{(\omega_{\underset{\sim}{q}j}\,\omega_E^2)^2}$$

$$\times \sum_{\alpha\beta\gamma\lambda} q_\alpha q_\beta q_\gamma\, e_\alpha(-\underset{\sim}{q}j)\, e_\lambda(\underset{\sim}{q}j)$$

$$\times \left[F_{\alpha\beta\lambda}(\underset{\sim}{q}) - F_{\alpha\beta\lambda}(\underset{\sim}{q}_1) - F_{\alpha\beta\lambda}(\underset{\sim}{q}_2)\right] \qquad (5.41)$$

Replacing the Δ function by its plane wave representation (Eq. (5.5)) and using the condition given by Eq. (5.22), Eq. (5.41) reduces to

$$I_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) = \frac{-i\,2^{3/2}}{3\hbar^{3/2}\beta^{3}N^{1/2}M^{3/2}} \sum_{\alpha\beta\gamma\lambda} q_\alpha q_\beta q_\gamma \frac{e_\gamma(-\underset{\sim}{q}j)\,e_\lambda(\underset{\sim}{q}j)}{(\omega_{\underset{\sim}{q}j}\,\omega_E^{2})^{2}}$$

$$\times \left[N^{2} F_{\alpha\beta\lambda}(\underset{\sim}{q}) - N\sum_{\underset{\sim}{q}_1} F_{\alpha\beta\lambda}(\underset{\sim}{q}_1) - N\sum_{\underset{\sim}{q}_2} F_{\alpha\beta\lambda}(\underset{\sim}{q}_2) \right] \tag{5.42}$$

According to Section 5.4, the two sums in the square bracket in Eq. (5.42) are identically zero and the final expression for $I_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j})$ as obtained from Eq. (5.42) is

$$I_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) = \frac{-i\,2^{3/2}}{3\hbar^{3/2}\beta^{3}N^{1/2}M^{3/2}} \sum_{\alpha\beta\gamma\lambda} q_\alpha q_\beta q_\gamma \frac{e_\gamma(-\underset{\sim}{q}j)\,e_\lambda(\underset{\sim}{q}j)}{(\omega_{\underset{\sim}{q}j}\,\omega_E^{2})^{2}} F_{\alpha\beta\lambda}(\underset{\sim}{q}) \tag{5.43}$$

Once again we observe that this final expression for the interference term contains no Brillouin Zone sum.

The contribution to the resistivity integrand arising from the I term requires the calculation to be performed for all values of $\underset{\sim}{q}$. This has been done and the numerical results for the I term contribution to ρ for Na and K, in the PEA are presented in Tables 9 and 11, respectively. In the TEA, the I term expression (Eq. (5.43)) further simplifies to the following:

$$I_{\underset{\sim}{q}j}(\omega_{\underset{\sim}{q}j}) = \frac{-i\,2^{3/2}N^{2}}{3\hbar^{3/2}\beta^{3}N^{1/2}M^{3/2}} \sum_{\alpha\beta\gamma\lambda} q_\alpha q_\beta q_\gamma \frac{e_\gamma(-\underset{\sim}{q}j)\,e_\lambda(\underset{\sim}{q}j)}{(\omega_E'\,\omega_E^{2})^{2}} F_{\alpha\beta\lambda}(\underset{\sim}{q}) \tag{5.44}$$

The contribution to ρ for Na and K from the I term in the TEA are presented in Tables 10 and 12, respectively.

6.0 DISCUSSION

In this section we present a discussion of the numerical results obtained for the various contributions to ρ obtained from the different physical processes such as the DW, MP term and the anharmonic effects (viz., CS, QS, W and I) under separate headings. The calculations have been done for Na and K in the high temperature limit in the temperature range Θ_D to the melting point (T_M). Θ_D and T_M for Na and K are given by

	Θ_D °K	T_M °K
Na	158	370.96
K	91	336.8

(a) The Debye-Waller and Multi-Phonon Results

The contribution to ρ for Na and K from the DW factor and the MP term along with the harmonic contributions ρ_H are represented in Tables 1 and 2, respectively. The DW and MP term contributions to ρ for Na and K are also presented graphically in Figures 1 and 2, respectively. For Na, the DW contribution decreases the value of ρ_H by 8 to 21% and the MP term contributions increase ρ_H by 10 to 26%. Thus, the overall contribution to ρ for Na from these two terms is 2 to 5% of the value of ρ_H. This is in disagreement with the conclusion of Reyes and Helman (1974) that the DW and MP term give a joint contribution to ρ_H for Na of 10% for $T \gtrsim \Theta_D$.

A similar pattern is seen for K where the contribution to ρ from the DW factor shows a reduction of 5 to 20% and the MP term contribution enhances the values of ρ_H by 21%. Hence, the overall increase in the value of ρ_H at T_M is 1%. This is in agreement with the conjecture made by Sham and Ziman (1963) that the cancellation between the DW factor and MP term might be complete.

Even though we have not presented the derivation of the higher order terms of the MP series in this thesis, we have done the derivation of the next two terms of the MP series (viz., the three- and four-phonon processes). In the high temperature limit the contributions to ρ from the three- and four-phonon processes vary as T^3 and T^4, respectively. The numerical evaluation of these contributions are found to be negligible. This indicates that there is hardly any contribution to ρ from the MP terms higher than T^2 in the high temperature limit.

(b) The Cubic and Quartic Shift Results

The contributions from the CS and QS to ρ are presented in Tables 3, 4 and 5, and Figure 3 for Na and Tables 6, 7 and 8, and Figure 4 for K.

The exact calculation shows that the QS contribution to ρ reduces the values of ρ_H by 5 to 14% for Na and 2 to 9% for K. As mentioned in Section 5.4, we expect the CS and QS contributions to ρ to cancel each other based on the comparison made in Table 15. In Table 15, we present the QS contribution to the phonon frequencies obtained by numerically evaluating Eq. (4.5) and the CS contribution to the phonon frequencies obtained by Glyde and Taylor (1971). It is obvious that the CS computed by Glyde and Taylor (1971) would not be the same as the CS obtained from Eq. (5.17) due to the fact that they have used the self-consistent phonon theory to calculate $\omega_{\underset{\sim}{q}j}$ and $\underset{\sim}{\varepsilon}_{\underset{\sim}{q}j}$ and the average value of

$\Phi_{\alpha\beta\gamma}$, i.e., $\langle\Phi_{\alpha\beta\gamma}\rangle$. We have compared the values of the QS obtained from Eq. (4.5) to the difference of the quasiharmonic and self-consistent harmonic theory results obtained by Glyde and Taylor (1971) and found the agreement very good which indicates that terms higher than the QS are negligible. From this we can conclude that if the CS is calculated from Eq. (5.17), it would be almost the same as the CS obtained by Glyde and Taylor (1971). This would imply the cancellation of the QS and CS contributions to ρ if computed exactly.

To estimate the extent of cancellation between the CS and QS, we have computed the two shifts in the partial Einstein approximation (PEA) and the total Einstein approximation (TEA).

In the PEA, the CS contribution to ρ increases the value of ρ_H by 5 to 14% for Na and 3 to 11% for K while the QS contribution to ρ decreases the value of ρ_H by 4 to 11% for Na and 2 to 6% for K. Thus the overall change in the value of ρ_H is 1 to 3% for Na and 1 to 5% for K. In the TEA, the value of ρ_H for Na and K changes by 8 to 20% and 3 to 14%, respectively, due to the CS contribution while the QS contribution changes the value of ρ_H by -8 to -21% for Na and -3 to -13% for K. This gives for ρ_H an overall reduction of 1% in Na and increase of 1% in K at the melting temperature. We find a strong cancellation between the CS and QS contributions to ρ_H for Na and K, in PEA and TEA calculations.

(c) The Width and Interference Results

The contribution to ρ from the W and I terms in the PEA are presented in Table 9 and Figure 5 for Na and Table 11 and Figure 6 for

K. In the PEA, the W contribution changes the value of ρ for Na and K by 6 to 14% and 3 to 11%, respectively, while the I term contribution changes the value of ρ_H for Na and K by -5 to -12% and -3 to -10%. This gives an overall change in ρ_H of 1 to 2% for Na and 0 to 1% for K.

The W and I term contributions to ρ in TEA are presented in Table 12 and Figure 5 for Na and Table 13 and Figure 6 for K. For Na the W contribution changes the value of ρ_H by 6 to 15% and the I term changes the value of ρ_H by -5 to -12% giving an overall increase in ρ_H of 1 to 3%. The W contribution changes the value of ρ_H for K by 3 to 11% while the I term contribution changes ρ_H by -3 to -10% giving once again an overall increase in ρ_H of 0 to 1% in the TEA. Here again we have a strong cancellation between the contribution to ρ from the W and I terms.

The total contribution to ρ arising from the exact calculation (harmonic, DW and MP terms) and the approximate calculation (QS, CS, W and I) in the PEA and TEA for Na and K is presented in Tables 13 and 14 and Figures 7 and 8, respectively. In the high temperature limit we can express ρ as

$$\rho = AT + BT^2 \tag{6.1}$$

where the constants A and B in units of $\Omega \cdot$m for Na and K in the PEA and TEA are given by:

	A	B_{PEA}	B_{TEA}
Na	1.2761×10^{-10}	3.7803×10^{-14}	2.3376×10^{-14}
K	1.7904×10^{-10}	3.5197×10^{-14}	2.1141×10^{-14}

In the PEA, the overall increase in ρ_H for Na and K due to the BT^2 term in Eq. (6.1) is 4 to 11% and 2 to 7%, respectively, while in the TEA the increase from this term in ρ_H is 3 to 7% for Na and 1 to 4% for K. This is in disagreement with the conclusion of Grimwall (1973) that the T^2 contribution to ρ would be of the order of -10%.

Caption for Tables

The percentage differences in the tables are obtained by the use of the following formula:

$$\frac{\rho_o - \rho_H}{\rho_H} \times 100 = \%\ \text{Diff.}$$

where ρ_H is the harmonic resistivity and ρ_o is the corresponding resistivity obtained by adding the T^2 contribution to the harmonic resistivity (ρ_H).

Table 1. The Debye-Waller and Multi-phonon contributions to ρ for Na ($a = 4.225 \times 10^{-8}$cm) in units of $10^{-8}\,\Omega$ m

T °K	ρ_H	ρ_{DW}	%Diff	ρ_{MP}	%Diff	ρ_T	%Diff
150	1.9141	-0.1596	-8.33	0.1996	10.42	1.9541	2.08
160	2.0417	-0.1816	-8.89	0.2271	11.12	2.0872	2.22
170	2.1693	-0.2050	-9.45	0.2563	11.81	2.2206	2.36
180	2.2969	-0.2298	-10.00	0.2874	12.51	2.3545	2.50
190	2.4245	-0.2561	-10.56	0.3202	13.20	2.4887	2.64
200	2.5521	-0.2837	-11.11	0.3548	13.90	2.6232	2.78
210	2.6797	-0.3128	-11.67	0.3912	14.59	2.7581	2.92
220	2.8073	-0.3433	-12.23	0.4293	15.29	2.8933	3.06
230	2.9350	-0.3752	-12.78	0.4692	15.98	3.0289	3.20
240	3.0626	-0.4086	-13.34	0.5109	16.68	3.1649	3.34
250	3.1902	-0.4434	-13.89	0.5544	17.37	3.3012	3.48
260	3.3178	-0.4795	-14.45	0.5996	18.07	3.4379	3.61
270	3.4454	-0.5171	-15.01	0.6467	18.76	3.5749	3.75
280	3.5730	-0.5562	-15.56	0.6955	19.46	3.7123	3.89
290	3.7006	-0.5966	-16.12	0.7460	20.16	3.8500	4.03
300	3.8282	-0.6385	-16.67	0.7984	20.85	3.9881	4.17
310	3.9558	-0.6817	-17.23	0.8525	21.55	4.1266	4.31
320	4.0834	-0.7264	-17.79	0.9084	22.24	4.2654	4.45
330	4.2110	-0.7725	-18.34	0.9660	22.94	4.4045	4.59
340	4.3387	-0.8201	-18.90	1.0255	23.63	4.5440	4.73
350	4.4663	-0.8690	-19.45	1.0867	24.33	4.6839	4.87
360	4.5939	-0.9194	-20.01	1.1497	25.02	4.8241	5.01
370	4.7215	-0.9712	-20.57	1.2144	25.72	4.9647	5.15

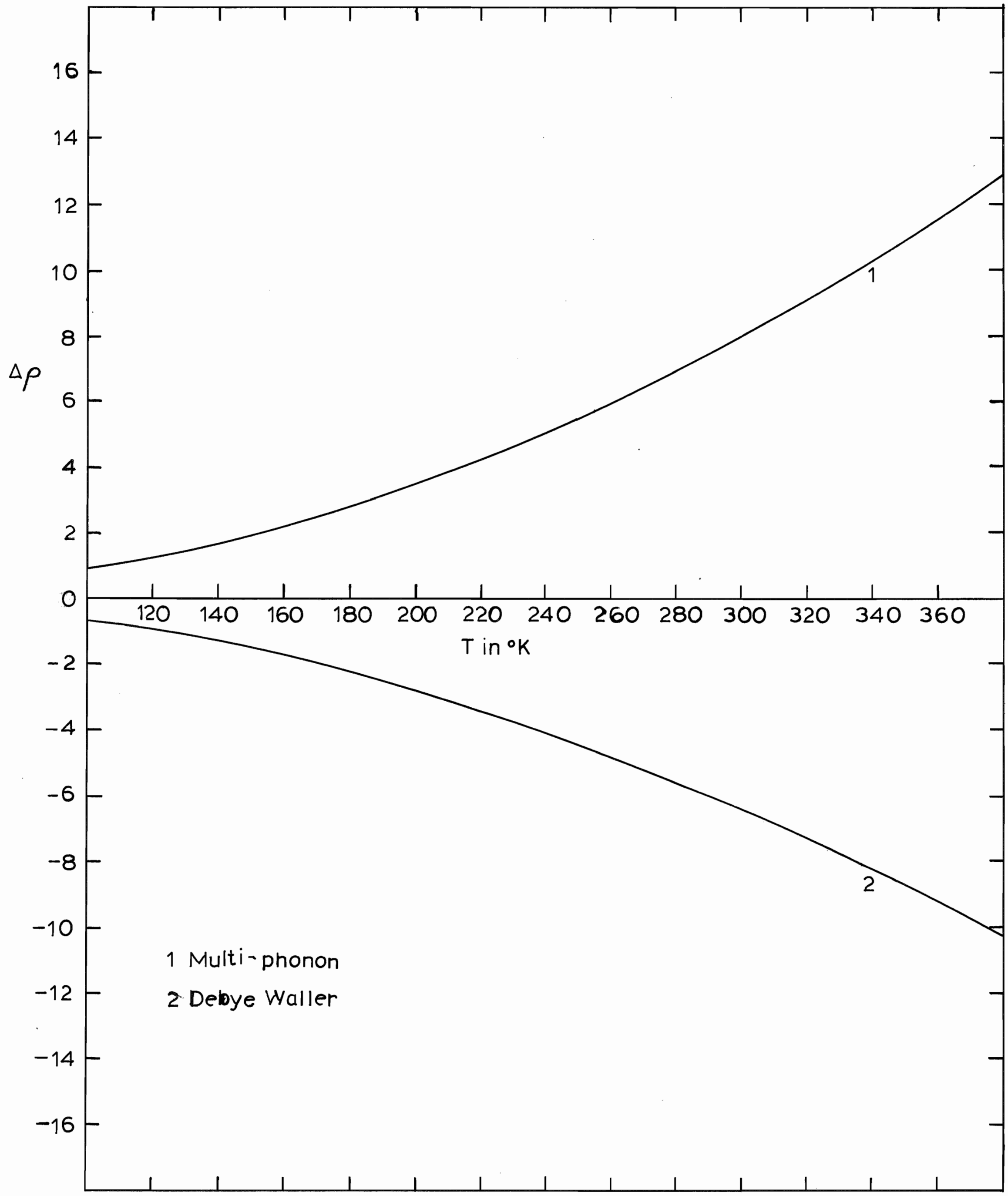


Figure 1. The Debye-Waller and Multi-phonon correction to ρ for Na ($a = 4.225 \times 10^{-8}$ cm) as a function of temperature. $\Delta\rho$ is in units of $10^{-9}\,\Omega$ m

Table 2. The Debye-Waller and Multi-phonon contributions to ρ for K ($a = 5.233 \times 10^{-8}$cm) in units of $10^{-8}\Omega$ m

T °K	ρ_H	ρ_{DW}	%Diff	ρ_{MP}	%Diff	ρ_T	%Diff
90	1.6113	-0.0861	-5.34	0.0915	5.68	1.6167	0.33
100	1.7904	-0.1064	-5.94	0.1130	6.31	1.7970	0.36
110	1.9694	-0.1287	-6.53	0.1367	6.94	1.9774	0.40
120	2.1485	-0.1532	-7.13	0.1627	7.57	2.1580	0.44
130	2.3275	-0.1798	-7.72	0.1910	8.20	2.3387	0.47
140	2.5065	-0.2085	-8.32	0.2215	8.83	2.5195	0.51
150	2.6856	-0.2394	-8.91	0.2542	9.46	2.7005	0.55
160	2.8646	-0.2724	-9.50	0.2893	10.09	2.8815	0.59
170	3.0437	-0.3075	-10.10	0.3266	10.73	3.0628	0.62
180	3.2227	-0.3447	-10.69	0.3661	11.36	3.2441	0.66
190	3.4018	-0.3841	-11.29	0.4080	11.99	3.4256	0.70
200	3.5808	-0.4256	-11.88	0.4520	12.62	3.6072	0.73
210	3.7598	-0.4692	-12.48	0.4984	13.25	3.7890	0.77
220	3.9389	-0.5150	-13.07	0.5470	13.88	3.9709	0.81
230	4.1179	-0.5629	-13.66	0.5978	14.51	4.1529	0.84
240	4.2970	-0.6129	-14.26	0.6509	15.14	4.3350	0.88
250	4.4760	-0.6650	-14.85	0.7063	15.78	4.5173	0.92
260	4.6550	-0.7193	-15.45	0.7640	16.41	4.6997	0.95
270	4.8341	-0.7757	-16.04	0.8239	17.04	4.8823	0.99
280	5.0131	-0.8342	-16.64	0.8860	17.67	5.0650	1.03
290	5.1922	-0.8949	-17.23	0.9505	18.30	5.2478	1.07
300	5.3712	-0.9576	-17.82	1.0171	18.93	5.4307	1.10
310	5.5503	-1.0225	-18.42	1.0861	19.56	5.6138	1.14
320	5.7293	-1.0896	-19.01	1.1573	20.19	5.7970	1.18
330	5.9083	-1.1588	-19.61	1.2307	20.83	5.9803	1.21
340	6.0874	-1.2300	-20.20	1.3065	21.46	6.1638	1.25

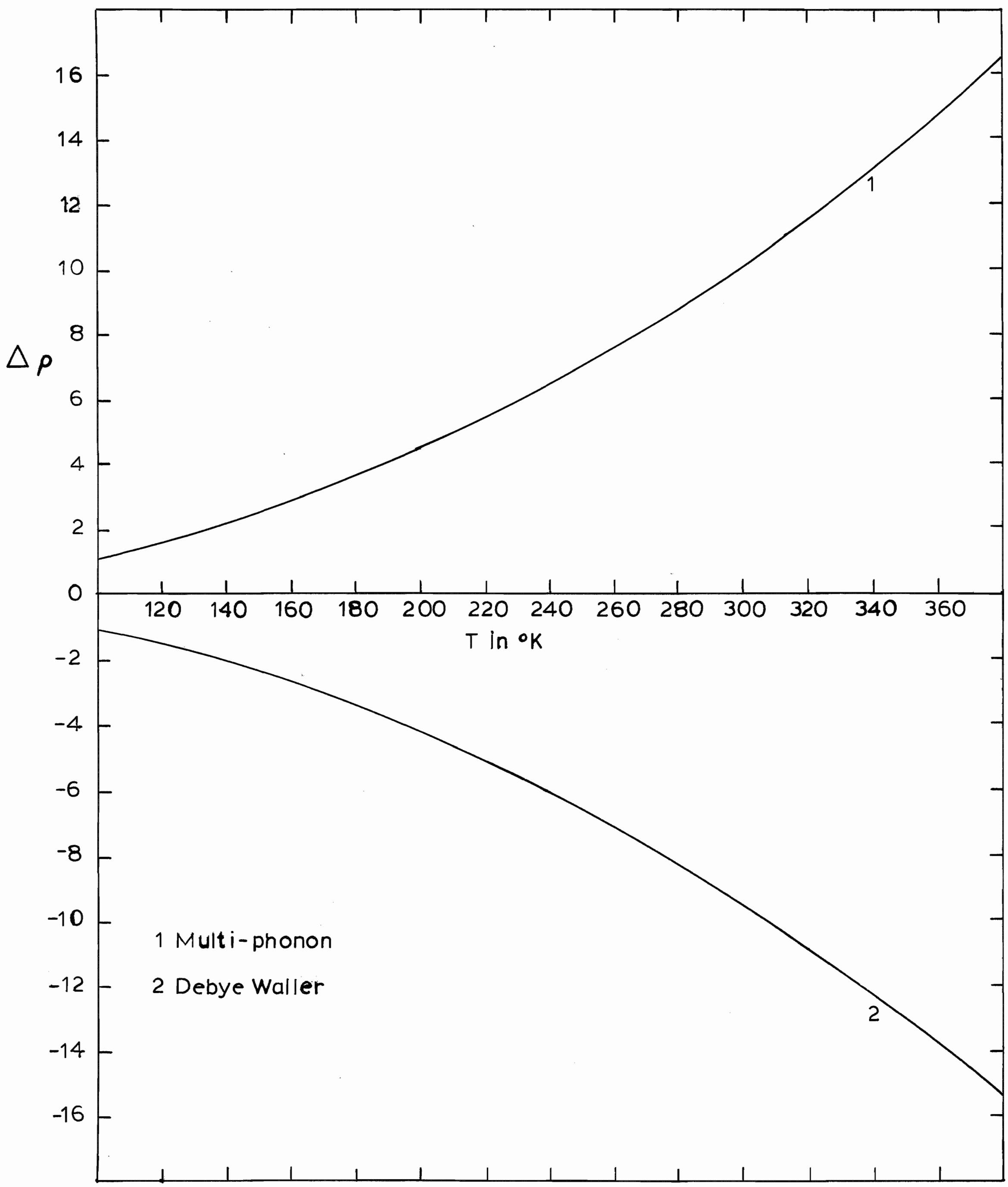


Figure 2. The Debye Waller and Multi-phonon correction to ρ for K ($a = 5.233 \times 10^{-8}$ cm) as a function of temperature.
$\Delta\rho$ is in units of $10^{-9}\,\Omega$ m

Table 3. The Quartic Shift contribution to ρ for Na ($a = 4.225 \times 10^{-8}$cm) in units of $10^{-8}\Omega$ m

T °K	ρ_H	ρ_{QS}	ρ_T	%Diff
150	1.9141	-0.1043	1.8098	-5.45
160	2.0417	-0.1187	1.9230	-5.81
170	2.1693	-0.1340	2.0353	-6.17
180	2.2969	-0.1502	2.1467	-6.54
190	2.4245	-0.1673	2.2571	-6.90
200	2.5521	-0.1854	2.3667	-7.26
210	2.6797	-0.2044	2.4753	-7.63
220	2.8073	-0.2244	2.5829	-7.99
230	2.9350	-0.2452	2.6897	-8.35
240	3.0626	-0.2670	2.7955	-8.72
250	3.1902	-0.2898	2.9004	-9.08
260	3.3178	-0.3134	3.0043	-9.44
270	3.4454	-0.3380	3.1074	-9.81
280	3.5730	-0.3635	3.2095	-10.17
290	3.7006	-0.3899	3.3107	-10.53
300	3.8282	-0.4173	3.4109	-10.90
310	3.9558	-0.4455	3.5102	-11.26
320	4.0834	-0.4748	3.6086	-11.62
330	4.2110	-0.5049	3.7061	-11.99
340	4.3387	-0.5360	3.8026	-12.35
350	4.4663	-0.5680	3.8983	-12.71
360	4.5939	-0.6009	3.9929	-13.08
370	4.7215	-0.6347	4.0867	-13.44

Table 4. The Cubic and Quartic Shift contributions to ρ for Na ($a = 4.225 \times 10^{-8}$cm) in units of $10^{-8}\Omega$ m in the PEA

T °K	ρ_H	ρ_{CS}	%Diff	ρ_{QS}	%Diff	ρ_T	%Diff
150	1.9141	0.1072	5.60	-0.0839	-4.38	1.9373	1.21
160	2.0417	0.1219	5.97	-0.0955	-4.67	2.0681	1.29
170	2.1693	0.1376	6.34	-0.1078	-4.97	2.1991	1.37
180	2.2969	0.1543	6.72	-0.1209	-5.26	2.3304	1.45
190	2.4245	0.1720	7.09	-0.1347	-5.55	2.4618	1.53
200	2.5521	0.1905	7.46	-0.1492	-5.84	2.5934	1.61
210	2.6797	0.2101	7.84	-0.1646	-6.14	2.7253	1.69
220	2.8073	0.2306	8.21	-0.1806	-6.43	2.8573	1.77
230	2.9350	0.2520	8.58	-0.1974	-6.72	2.9896	1.86
240	3.0626	0.2744	8.96	-0.2149	-7.01	3.1220	1.94
250	3.1902	0.2977	9.33	-0.2332	-7.31	3.2547	2.02
260	3.3178	0.3220	9.70	-0.2523	-7.60	3.3876	2.10
270	3.4454	0.3473	10.08	-0.2720	-7.89	3.5206	2.18
280	3.5730	0.3735	10.45	-0.2926	-8.18	3.6539	2.26
290	3.7006	0.4007	10.82	-0.3138	-8.48	3.7874	2.34
300	3.8282	0.4288	11.20	-0.3359	-8.77	3.9211	2.42
310	3.9558	0.4578	11.57	-0.3586	-9.06	4.0550	2.50
320	4.0834	0.4879	11.94	-0.3822	-9.35	4.1891	2.58
330	4.2110	0.5188	12.32	-0.4064	-9.65	4.3235	2.66
340	4.3387	0.5507	12.69	-0.4314	-9.94	4.4580	2.75
350	4.4663	0.5836	13.06	-0.4572	-10.23	4.5927	2.83
360	4.5939	0.6174	13.44	-0.4837	-10.52	4.7277	2.91
370	4.7215	0.6522	13.81	-0.5109	-10.82	4.8628	2.99

Table 5. The Cubic and Quartic Shift contributions to ρ for Na ($a = 4.225 \times 10^{-8}$cm) in units of $10^{-8}\Omega$ m in the TEA

T °K	ρ_H	ρ_{CS}	%Diff	ρ_{QS}	%Diff	ρ_T	%Diff
150	1.9141	0.1537	8.03	-0.1661	-8.67	1.9017	-0.64
160	2.0417	0.1748	8.56	-0.1890	-9.25	2.0276	-0.69
170	2.1693	0.1974	9.10	-0.2133	-9.83	2.1534	-0.73
180	2.2969	0.2213	9.63	-0.2392	-10.41	2.2790	-0.77
190	2.4245	0.2466	10.17	-0.2665	-10.99	2.4046	-0.82
200	2.5521	0.2732	10.70	-0.2953	-11.57	2.5301	-0.86
210	2.6797	0.3012	11.24	-0.3256	-12.15	2.6554	-0.90
220	2.8073	0.3306	11.77	-0.3573	-12.72	2.7806	-0.95
230	2.9350	0.3613	12.31	-0.3905	-13.30	2.9058	-0.99
240	3.0626	0.3934	12.84	-0.4252	-13.88	3.0308	-1.03
250	3.1902	0.4269	13.38	-0.4614	-14.46	3.1557	-1.08
260	3.3178	0.4618	13.91	-0.4991	-15.04	3.2805	-1.12
270	3.4454	0.4980	14.45	-0.5382	-15.62	3.4052	-1.16
280	3.5730	0.5355	14.98	-0.5788	-16.20	3.5297	-1.21
290	3.7006	0.5745	15.52	-0.6209	-16.77	3.6542	-1.25
300	3.8282	0.6148	16.06	-0.6645	-17.35	3.7786	-1.29
310	3.9558	0.6565	16.59	-0.7095	-17.93	3.9028	-1.34
320	4.0834	0.6995	17.13	-0.7560	-18.51	4.0269	-1.38
330	4.2110	0.7439	17.66	-0.8040	-19.09	4.1509	-1.42
340	4.3387	0.7897	18.20	-0.8535	-19.67	4.2749	-1.47
350	4.4663	0.8368	18.73	-0.9044	-20.25	4.3987	-1.51
360	4.5939	0.8853	19.27	-0.9568	-20.82	4.5223	-1.55
370	4.7215	0.9352	19.80	-1.0107	-21.40	4.6459	-1.60

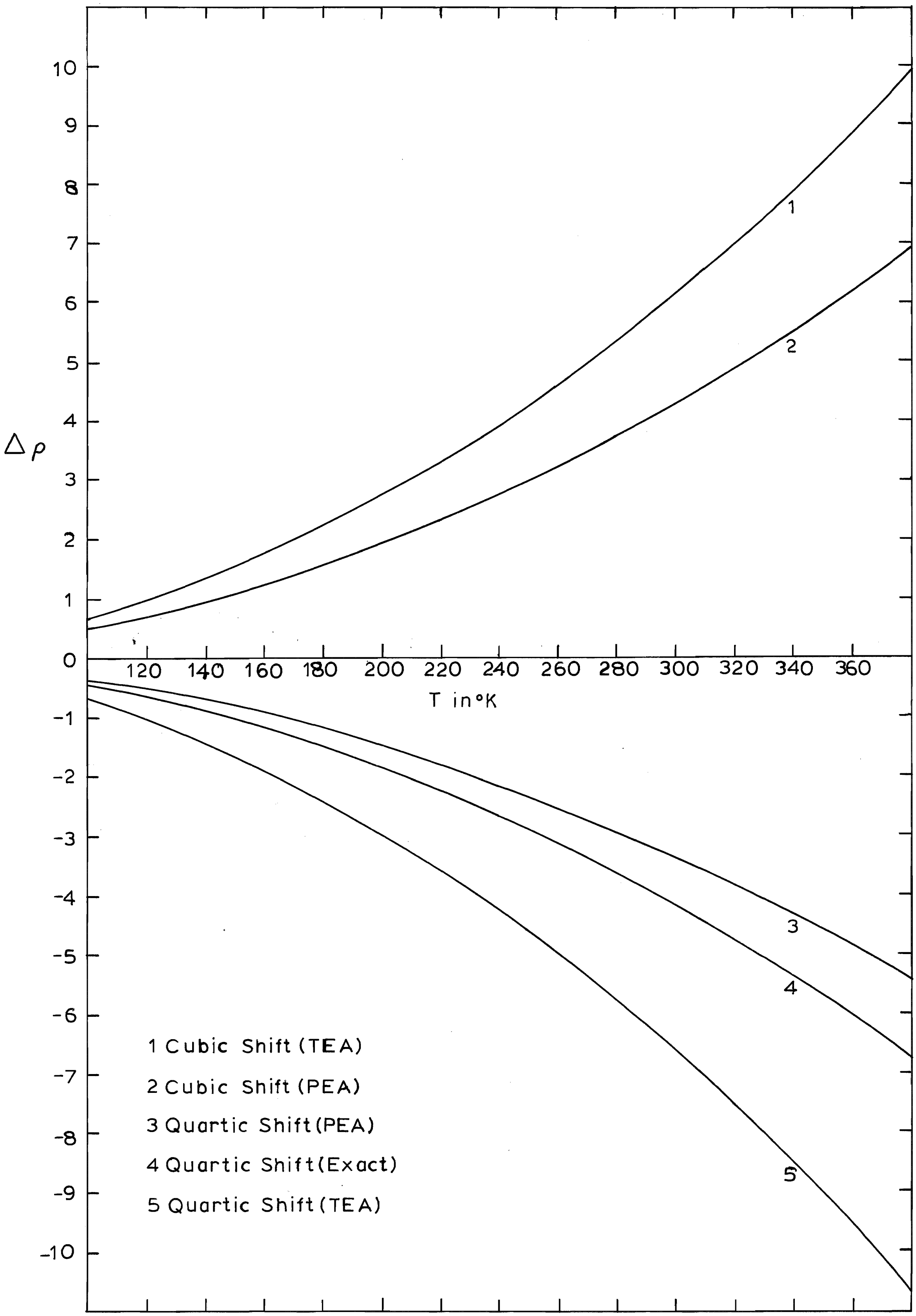


Figure 3. The Cubic and Quartic Shift contribution to ρ for Na ($a = 4.225 \times 10^{-8}$ cm) as a function of temperature. $\Delta\rho$ is in units of $10^{-9}\,\Omega$ m

Table 6. The Quartic Shift contribution to ρ for K ($a = 5.223 \times 10^{-8}$cm) in units of $10^{-8}\Omega$ m

T °K	ρ_H	ρ_{QS}	ρ_T	%Diff
90	1.6113	-0.0394	1.5718	-2.45
100	1.7904	-0.0487	1.7416	-2.72
110	1.9694	-0.0589	1.9104	-2.99
120	2.1485	-0.0701	2.0783	-3.26
130	2.3275	-0.0823	2.2451	-3.53
140	2.5065	-0.0955	2.4110	-3.81
150	2.6856	-0.1096	2.5759	-4.08
160	2.8646	-0.1247	2.7398	-4.35
170	3.0437	-0.1408	2.9028	-4.62
180	3.2227	-0.1579	3.0648	-4.90
190	3.4018	-0.1759	3.2258	-5.17
200	3.5808	-0.1949	3.3858	-5.44
210	3.7598	-0.2149	3.5449	-5.71
220	3.9389	-0.2359	3.7029	-5.99
230	4.1179	-0.2578	3.8600	-6.26
240	4.2970	-0.2807	4.0162	-6.53
250	4.4760	-0.3046	4.1713	-6.80
260	4.6550	-0.3295	4.3255	-7.07
270	4.8341	-0.3553	4.4787	-7.35
280	5.0131	-0.3821	4.6309	-7.62
290	5.1922	-0.4099	4.7822	-7.89
300	5.3712	-0.4387	4.9325	-8.16
310	5.5503	-0.4684	5.0818	-8.44
320	5.7293	-0.4991	5.2301	-8.71
330	5.9083	-0.5308	5.3775	-8.98
340	6.0874	-0.5635	5.5239	-9.25

Table 7. The Cubic and Quartic Shift contributions to ρ for K ($a = 5.233 \times 10^{-8}$cm) in units of $10^{-8}\Omega$ m in the PEA

T °K	ρ_H	ρ_{CS}	%Diff	ρ_{QS}	%Diff	ρ_T	%Diff
90	1.6113	0.0467	2.90	-0.0253	-1.57	1.6328	1.33
100	1.7904	0.0577	3.22	-0.0312	-1.74	1.8169	1.47
110	1.9694	0.0698	3.54	-0.0377	-1.91	2.0015	1.62
120	2.1485	0.0831	3.86	-0.0449	-2.09	2.1866	1.77
130	2.3275	0.0975	4.19	-0.0527	-2.26	2.3723	1.92
140	2.5065	0.1131	4.51	-0.0612	-2.44	2.5585	2.07
150	2.6856	0.1298	4.83	-0.0702	-2.61	2.7452	2.21
160	2.8646	0.1477	5.15	-0.0799	-2.79	2.9324	2.36
170	3.0437	0.1668	5.48	-0.0902	-2.96	3.1202	2.51
180	3.2227	0.1870	5.80	-0.1012	-3.14	3.3085	2.66
190	3.4018	0.2084	6.12	-0.1127	-3.31	3.4974	2.81
200	3.5808	0.2309	6.44	-0.1249	-3.48	3.6868	2.95
210	3.7598	0.2545	6.77	-0.1377	-3.66	3.8767	3.10
220	3.9389	0.2794	7.09	-0.1511	-3.83	4.0671	3.25
230	4.1179	0.3054	7.41	-0.1652	-4.01	4.2581	3.40
240	4.2970	0.3325	7.73	-0.1799	-4.18	4.4496	3.55
250	4.4760	0.3608	8.06	-0.1952	-4.36	4.6416	3.69
260	4.6550	0.3902	8.38	-0.2111	-4.53	4.8341	3.84
270	4.8341	0.4208	8.70	-0.2277	-4.71	5.0272	3.99
280	5.0131	0.4526	9.02	-0.2449	-4.88	5.2208	4.14
290	5.1922	0.4855	9.35	-0.2627	-5.05	5.4150	4.29
300	5.3712	0.5195	9.67	-0.2811	-5.23	5.6097	4.43
310	5.5503	0.5548	9.99	-0.3002	-5.40	5.8049	4.58
320	5.7293	0.5911	10.31	-0.3198	-5.58	6.0006	4.73
330	5.9083	0.6287	10.64	-0.3401	-5.75	6.1969	4.88
340	6.0874	0.6673	10.96	-0.3611	-5.93	6.3936	5.03

Table 8. The Cubic and Quartic Shift contributions to ρ for K ($a = 5.233 \times 10^{-8}$cm) in units of $10^{-8}\Omega$ m in the TEA

T °K	ρ_H	ρ_{CS}	%Diff	ρ_{QS}	%Diff	ρ_T	%Diff
90	1.6113	0.0608	3.77	-0.0531	-3.29	1.6190	0.47
100	1.7904	0.0751	4.19	-0.0656	-3.66	1.7999	0.53
110	1.9694	0.0909	4.61	-0.0794	-4.03	1.9809	0.58
120	2.1485	0.1082	5.03	-0.0945	-4.39	2.1622	0.63
130	2.3275	0.1270	5.45	-0.1109	-4.76	2.3436	0.69
140	2.5065	0.1473	5.87	-0.1286	-5.13	2.5252	0.74
150	2.6856	0.1691	6.29	-0.1477	-5.49	2.7070	0.79
160	2.8646	0.1924	6.71	-0.1680	-5.86	2.8890	0.85
170	3.0437	0.2172	7.13	-0.1897	-6.23	3.0712	0.90
180	3.2227	0.2435	7.55	-0.2126	-6.59	3.2536	0.95
190	3.4018	0.2713	7.97	-0.2369	-6.96	3.4361	1.01
200	3.5808	0.3006	8.39	-0.2625	-7.33	3.6189	1.06
210	3.7598	0.3314	8.81	-0.2894	-7.69	3.8018	1.11
220	3.9389	0.3638	9.23	-0.3177	-8.06	3.9850	1.17
230	4.1179	0.3976	9.65	-0.3472	-8.43	4.1683	1.22
240	4.2970	0.4329	10.07	-0.3781	-8.79	4.3518	1.27
250	4.4760	0.4697	10.49	-0.4102	-9.16	4.5355	1.32
260	4.6550	0.5081	10.91	-0.4437	-9.53	4.7194	1.38
270	4.8341	0.5479	11.33	-0.4785	-9.89	4.9035	1.43
280	5.0131	0.5893	11.75	-0.5146	-10.26	5.0878	1.48
290	5.1922	0.6321	12.17	-0.5520	-10.63	5.2723	1.54
300	5.3712	0.6765	12.59	-0.5908	-10.99	5.4569	1.59
310	5.5503	0.7223	13.01	-0.6308	-11.36	5.6418	1.64
320	5.7293	0.7697	13.43	-0.6722	-11.73	5.8268	1.70
330	5.9083	0.8185	13.85	-0.7148	-12.09	6.0120	1.75
340	6.0874	0.8689	14.27	-0.7588	-12.46	6.1975	1.80

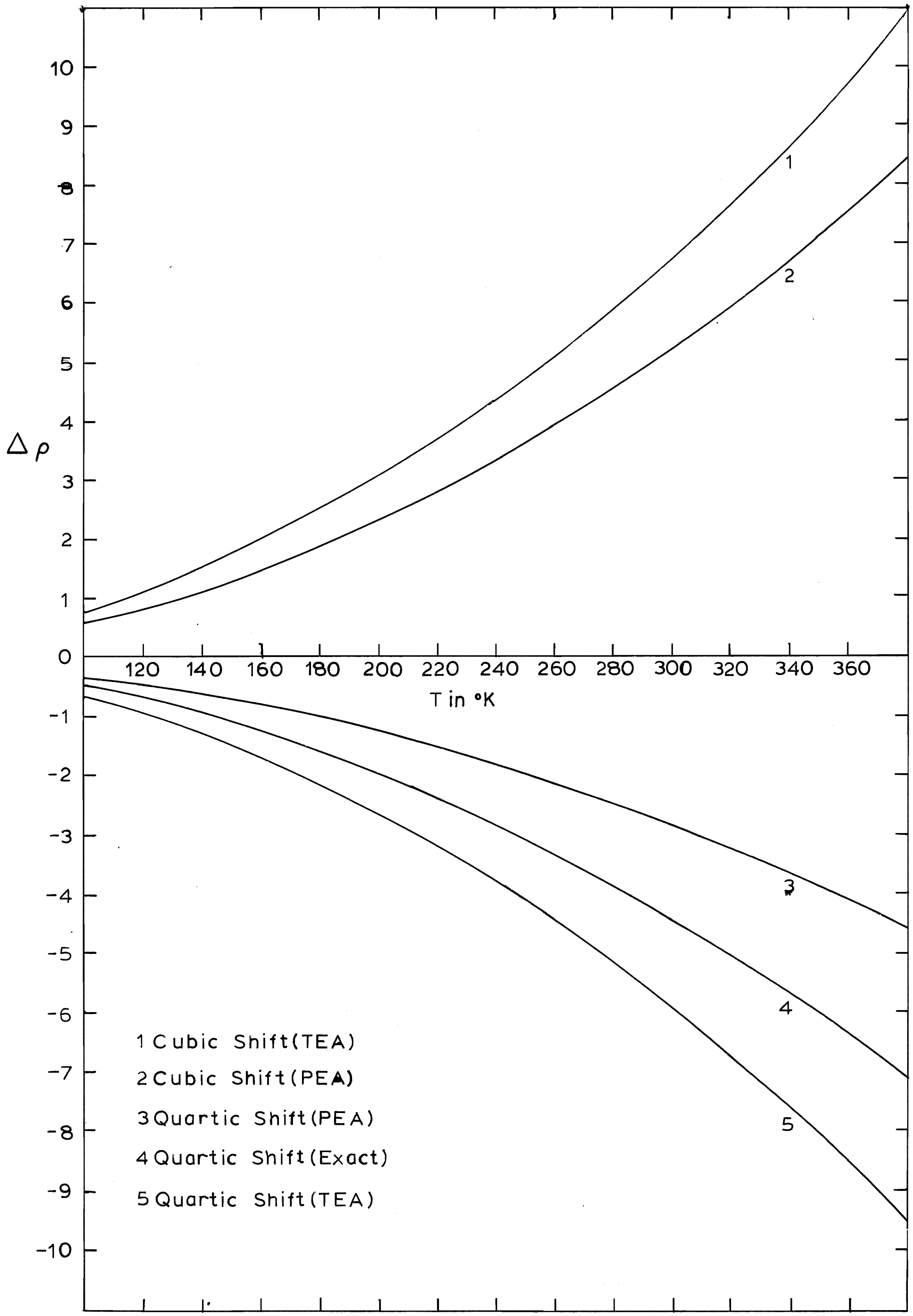


Figure 4. The Cubic and Quartic Shift contribution to ρ for K ($a = 5.233 \times 10^{-8}$ cm) as a function of temperature. $\Delta\rho$ is in units of $10^{-9}\,\Omega$ m

Table 9. The Width and Interference contributions to ρ for Na ($a = 4.225 \times 10^{-8}$cm) in units of $10^{-8}\Omega$ m in the PEA

T °K	ρ_H	ρ_W	%Diff	ρ_I	%Diff	ρ_T	%Diff
150	1.9141	0.1107	5.78	-0.0889	-4.64	1.9359	1.14
160	2.0417	0.1260	6.17	-0.1011	-4.95	2.0666	1.21
170	2.1693	0.1422	6.55	-0.1142	-5.26	2.1974	1.29
180	2.2969	0.1595	6.94	-0.1280	-5.57	2.3284	1.37
190	2.4245	0.1777	7.33	-0.1426	-5.88	2.4596	1.44
200	2.5521	0.1969	7.71	-0.1580	-6.19	2.5910	1.52
210	2.6797	0.2171	8.10	-0.1742	-6.50	2.7226	1.59
220	2.8073	0.2383	8.48	-0.1912	-6.81	2.8544	1.67
230	2.9350	0.2604	8.87	-0.2090	-7.12	2.9863	1.75
240	3.0626	0.2835	9.26	-0.2276	-7.43	3.1185	1.82
250	3.1902	0.3077	9.64	-0.2470	-7.74	3.2509	1.90
260	3.3178	0.3328	10.03	-0.2671	-8.05	3.3834	1.97
270	3.4454	0.3589	10.41	-0.2881	-8.36	3.5162	2.05
280	3.5730	0.3860	10.80	-0.3098	-8.67	3.6492	2.13
290	3.7006	0.4140	11.18	-0.3323	-8.98	3.7823	2.20
300	3.8282	0.4431	11.57	-0.3557	-9.29	3.9156	2.28
310	3.9558	0.4731	11.96	-0.3798	-9.60	4.0492	2.35
320	4.0834	0.5041	12.34	-0.4047	-9.91	4.1829	2.43
330	4.2110	0.5361	12.73	-0.4303	-10.22	4.3168	2.51
340	4.3387	0.5691	13.11	-0.4568	-10.53	4.4509	2.58
350	4.4663	0.6031	13.50	-0.4841	-10.84	4.5853	2.66
360	4.5939	0.6380	13.89	-0.5122	-11.14	4.7198	2.74
370	4.7215	0.6740	14.27	-0.5410	-11.45	4.8545	2.81

Table 10. The Width and Interference contributions to ρ for Na ($a = 4.225 \times 10^{-8}$ cm) in units of $10^{-8}\Omega$ m in the TEA

T °K	ρ_H	ρ_W	%Diff	ρ_I	%Diff	ρ_T	%Diff
150	1.9141	0.1186	6.20	-0.0936	-4.89	1.9391	1.30
160	2.0417	0.1350	6.61	-0.1065	-5.21	2.0702	1.39
170	2.1693	0.1524	7.02	-0.1202	-5.54	2.2015	1.48
180	2.2969	0.1709	7.44	-0.1348	-5.87	2.3330	1.56
190	2.4245	0.1904	7.85	-0.1502	-6.19	2.4647	1.65
200	2.5521	0.2109	8.26	-0.1664	-6.52	2.5966	1.74
210	2.6797	0.2326	8.68	-0.1835	-6.84	2.7288	1.83
220	2.8073	0.2553	9.09	-0.2014	-7.17	2.8612	1.91
230	2.9350	0.2790	9.50	-0.2201	-7.50	2.9938	2.00
240	3.0626	0.3038	9.92	-0.2397	-7.82	3.1267	2.09
250	3.1902	0.3296	10.33	-0.2601	-8.15	3.2597	2.18
260	3.3178	0.3565	10.74	-0.2813	-8.48	3.3930	2.26
270	3.4454	0.3845	11.16	-0.3034	-8.80	3.5265	2.35
280	3.5730	0.4135	11.57	-0.3263	-9.13	3.6602	2.44
290	3.7006	0.4436	11.98	-0.3500	-9.45	3.7942	2.52
300	3.8282	0.4747	12.40	-0.3745	-9.78	3.9284	2.61
310	3.9558	0.5069	12.81	-0.3999	-10.11	4.0628	2.70
320	4.0834	0.5401	13.22	-0.4262	-10.43	4.1974	2.79
330	4.2110	0.5744	13.64	-0.4532	-10.76	4.3322	2.87
340	4.3387	0.6097	14.05	-0.4811	-11.08	4.4673	2.96
350	4.4663	0.6461	14.46	-0.5098	-11.41	4.6026	3.05
360	4.5939	0.6836	14.88	-0.5394	-11.74	4.7381	3.13
370	4.7215	0.7221	15.29	-0.5697	-12.06	4.8738	3.22

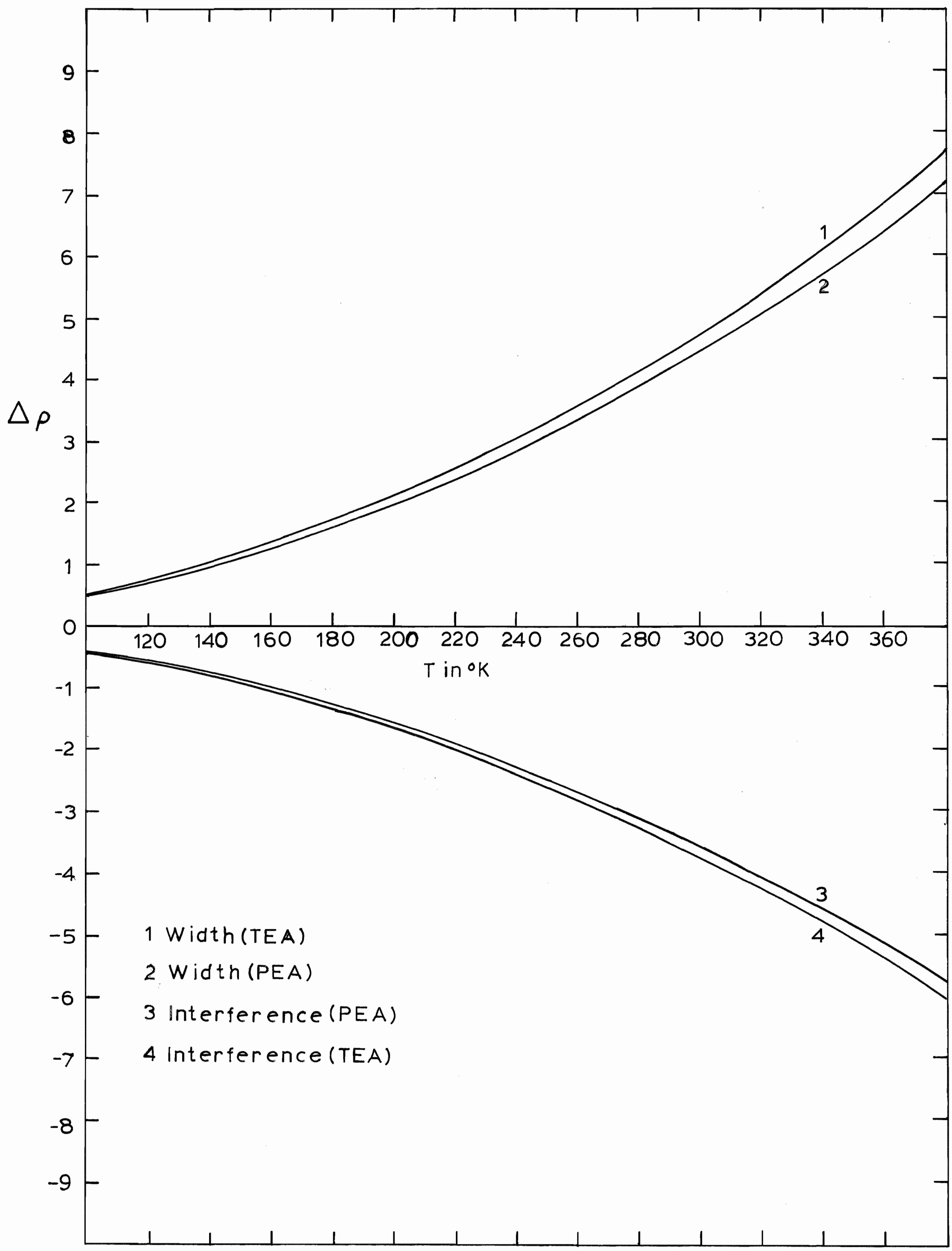


Figure 5. The Width and Interference contribution to ρ for Na ($a = 4.225 \times 10^{-8}$ cm) as a function of temperature. $\Delta\rho$ is in units of $10^{-9}\,\Omega$ m

Table 11. The Width and Interference contributions to ρ for K ($a = 5.223 \times 10^{-8}$cm) in units of $10^{-8}\Omega$ m in the PEA

T °K	ρ_H	ρ_W	%Diff	ρ_I	%Diff	ρ_T	%Diff
90	1.6113	0.0462	2.86	-0.0445	-2.76	1.6130	0.10
100	1.7904	0.0570	3.18	-0.0549	-3.07	1.7925	0.11
110	1.9694	0.0690	3.50	-0.0665	-3.37	1.9719	0.12
120	2.1485	0.0821	3.82	-0.0791	-3.68	2.1515	0.14
130	2.3275	0.0964	4.14	-0.0929	-3.99	2.3310	0.15
140	2.5065	0.1118	4.46	-0.1077	-4.29	2.5106	0.16
150	2.6856	0.1284	4.78	-0.1237	-4.60	2.6903	0.17
160	2.8646	0.1461	5.10	-0.1407	-4.91	2.8700	0.18
170	3.0437	0.1649	5.41	-0.1588	-5.22	3.0497	0.19
180	3.2227	0.1849	5.73	-0.1781	-5.52	3.2295	0.21
190	3.4018	0.2060	6.05	-0.1984	-5.83	3.4093	0.22
200	3.5808	0.2282	6.37	-0.2199	-6.14	3.5892	0.23
210	3.7598	0.2516	6.69	-0.2424	-6.44	3.7691	0.24
220	3.9389	0.2762	7.01	-0.2660	-6.75	3.9490	0.25
230	4.1179	0.3019	7.33	-0.2908	-7.06	4.1290	0.26
240	4.2970	0.3287	7.65	-0.3166	-7.36	4.3090	0.28
250	4.4760	0.3567	7.96	-0.3436	-7.67	4.4891	0.29
260	4.6550	0.3858	8.28	-0.3716	-7.98	4.6692	0.30
270	4.8341	0.4160	8.60	-0.4007	-8.29	4.8493	0.31
280	5.0131	0.4474	8.92	-0.4310	-8.59	5.0295	0.32
290	5.1922	0.4799	9.24	-0.4623	-8.90	5.2098	0.33
300	5.3712	0.5136	9.56	-0.4948	-9.21	5.3901	0.35
310	5.5503	0.5484	9.88	-0.5283	-9.51	5.5704	0.36
320	5.7293	0.5844	10.20	-0.5629	-9.82	5.7507	0.37
330	5.9083	0.6215	10.51	-0.5987	-10.13	5.9311	0.38
340	6.0874	0.6597	10.83	-0.6355	-10.44	6.1116	0.39

Table 12. The Width and Interference contributions to ρ for K ($a = 5.223 \times 10^{-8}$ cm) in units of $10^{-8}\,\Omega$ m in the TEA

T °K	ρ_H	ρ_W	%Diff	ρ_I	%Diff	ρ_T	%Diff
90	1.6113	0.0469	2.91	-0.0429	-2.66	1.6154	0.25
100	1.7904	0.0580	3.23	-0.0529	-2.96	1.7954	0.27
110	1.9694	0.0701	3.56	-0.0641	-3.25	1.9755	0.30
120	2.1485	0.0835	3.88	-0.0763	-3.55	2.1557	0.33
130	2.3275	0.0980	4.21	-0.0895	-3.84	2.3360	0.36
140	2.5065	0.1136	4.53	-0.1038	-4.14	2.5164	0.39
150	2.6856	0.1305	4.85	-0.1192	-4.44	2.6969	0.41
160	2.8646	0.1484	5.18	-0.1356	-4.73	2.8774	0.44
170	3.0437	0.1676	5.50	-0.1531	-5.03	3.0581	0.47
180	3.2227	0.1879	5.83	-0.1717	-5.32	3.2389	0.50
190	3.4018	0.2094	6.15	-0.1913	-5.62	3.4198	0.53
200	3.5808	0.2320	6.47	-0.2119	-5.92	3.6008	0.55
210	3.7598	0.2558	6.80	-0.2337	-6.21	3.7819	0.58
220	3.9389	0.2807	7.12	-0.2565	-6.51	3.9631	0.61
230	4.1179	0.3068	7.45	-0.2803	-6.80	4.1444	0.64
240	4.2970	0.3341	7.77	-0.3052	-7.10	4.3258	0.67
250	4.4760	0.3625	8.09	-0.3312	-7.40	4.5073	0.69
260	4.6550	0.3921	8.42	-0.3582	-7.69	4.6889	0.72
270	4.8341	0.4228	8.74	-0.3863	-7.99	4.8706	0.75
280	5.0131	0.4547	9.07	-0.4155	-8.28	5.0524	0.78
290	5.1922	0.4878	9.39	-0.4457	-8.58	5.2343	0.81
300	5.3712	0.5220	9.71	-0.4769	-8.88	5.4163	0.83
310	5.5503	0.5574	10.04	-0.5093	-9.17	5.5984	0.86
320	5.7293	0.5939	10.36	-0.5427	-9.47	5.7806	0.89
330	5.9083	0.6316	10.69	-0.5771	-9.76	5.9629	0.92
340	6.0874	0.6705	11.01	-0.6126	-10.06	6.1453	0.95

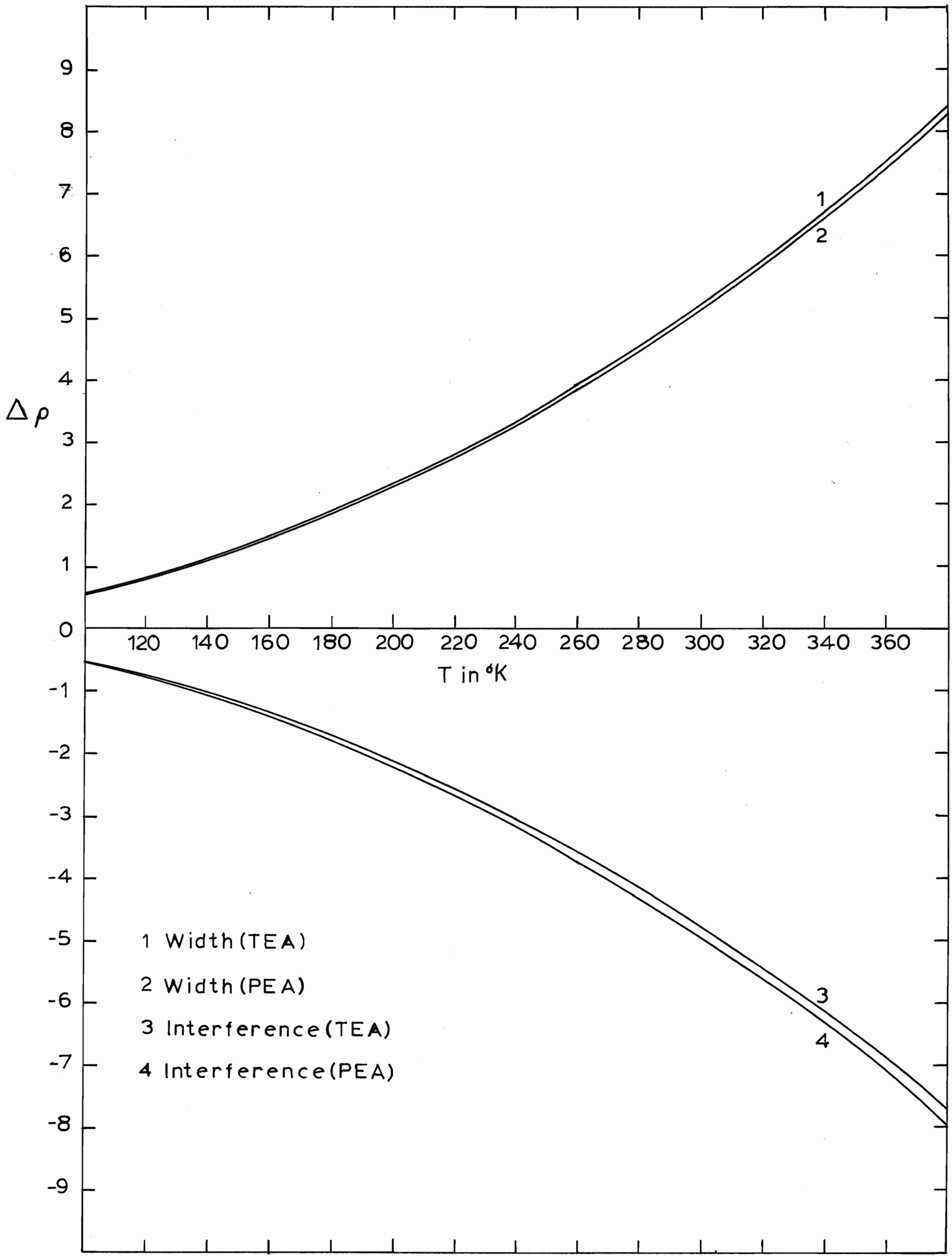


Figure 6. The Width and Interference contribution to ρ for K ($a = 5.233 \times 10^{-8}$ cm) as a function of temperature.
$\Delta\rho$ is in units of $10^{-9}\,\Omega\,m$

Table 13. The total T^2 contribution to ρ for Na ($a = 4.225 \times 10^{-8}$cm) in units of $10^{-8}\Omega$ m in the PEA and TEA

T °K	ρ_H	ρ_{PEA}	%Diff	ρ_{TEA}	%Diff
150	1.9141	1.9991	4.44	1.9667	2.74
160	2.0417	2.1385	4.73	2.1015	2.93
170	2.1693	2.2786	5.03	2.2369	3.11
180	2.2969	2.4194	5.33	2.3727	3.29
190	2.4245	2.5610	5.62	2.5089	3.48
200	2.5521	2.7033	5.92	2.6456	3.66
210	2.6797	2.8465	6.22	2.7828	3.84
220	2.8073	2.9903	6.51	2.9205	4.03
230	2.9350	3.1349	6.81	3.0586	4.21
240	3.0626	3.2803	7.10	3.1972	4.39
250	3.1902	3.4264	7.40	3.3363	4.57
260	3.3178	3.5733	7.70	3.4758	4.76
270	3.4454	3.7210	7.99	3.6158	4.94
280	3.5730	3.8694	8.29	3.7563	5.12
290	3.7006	4.0185	8.59	3.8972	5.31
300	3.8282	4.1684	8.88	4.0386	5.49
310	3.9558	4.3191	9.18	4.1805	5.67
320	4.0834	4.4705	9.47	4.3228	5.86
330	4.2110	4.6227	9.77	4.4656	6.04
340	4.3387	4.7757	10.07	4.6089	6.22
350	4.4663	4.9294	10.36	4.7526	6.41
360	4.5939	5.0838	10.66	4.8968	6.59
370	4.7215	5.2390	10.96	5.0415	6.77

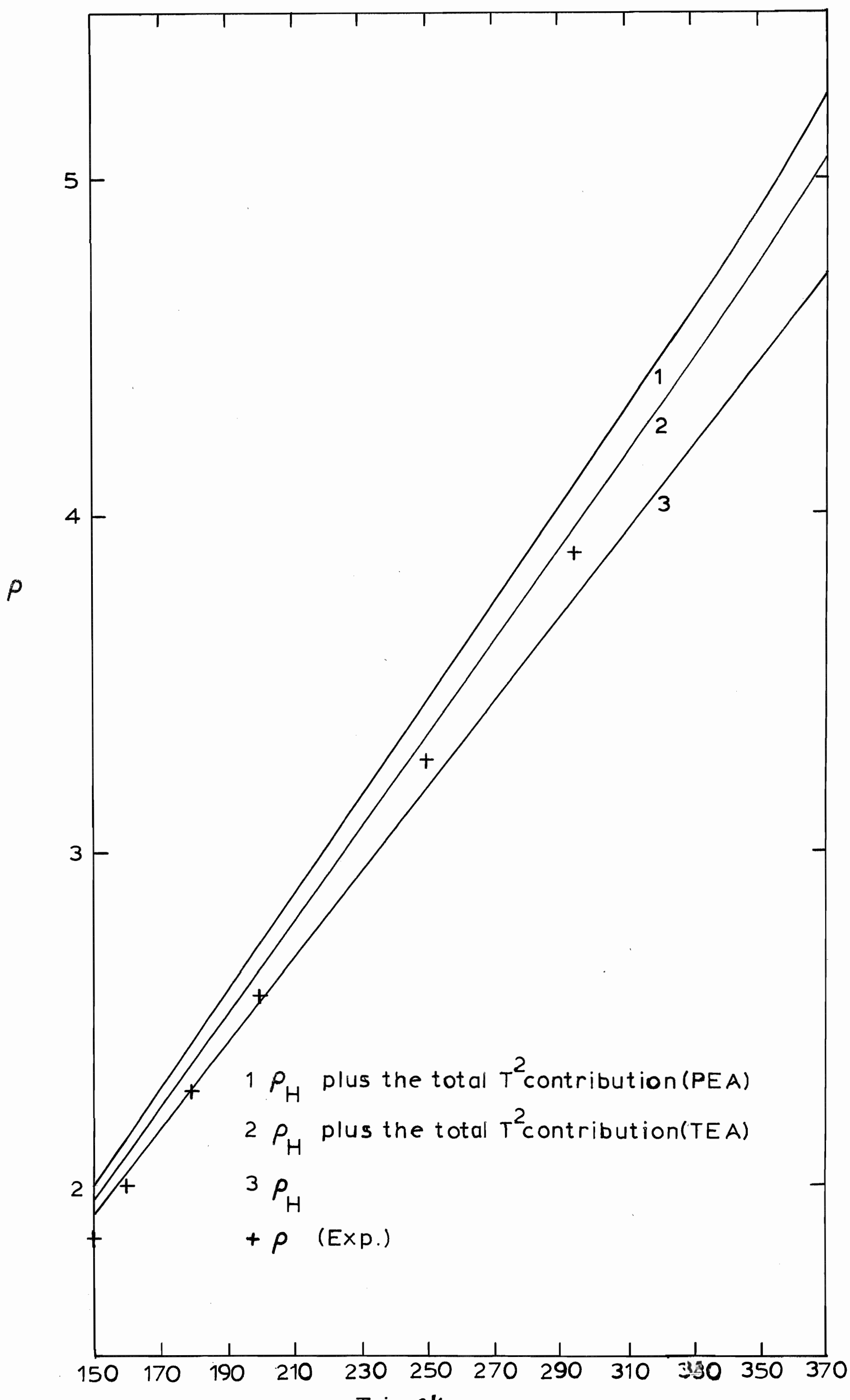
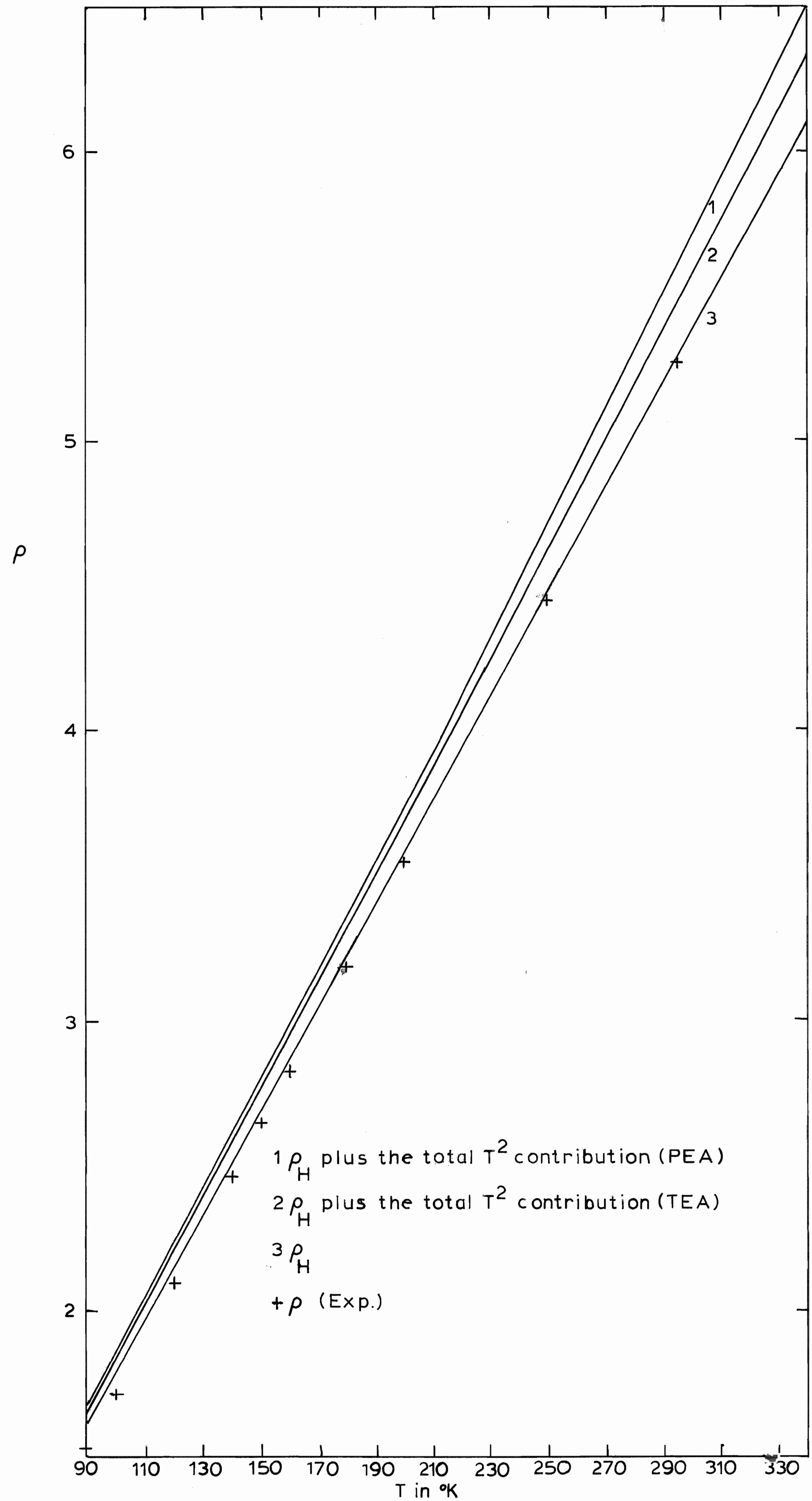


Figure 7. The total T^2 contribution to ρ for Na ($a = 4.225 \times 10^{-8}$ cm) in units of $10^{-9}\,\Omega$m as a function of temperature.

Table 14. The total T^2 contribution to ρ for K ($a = 5.223 \times 10^{-8}$cm) in units of $10^{-8}\Omega$ m in the PEA and TEA

T °K	ρ_H	ρ_{PEA}	%Diff	ρ_{TEA}	%Diff
90	1.6113	1.6398	1.76	1.6285	1.06
100	1.7904	1.8256	1.96	1.8115	1.18
110	1.9694	2.0120	2.16	1.9950	1.29
120	2.1485	2.1991	2.35	2.1789	1.41
130	2.3275	2.3870	2.55	2.3632	1.53
140	2.5065	2.5755	2.75	2.5480	1.65
150	2.6856	2.7648	2.94	2.7331	1.77
160	2.8646	2.9547	3.14	2.9187	1.88
170	3.0437	3.1454	3.34	3.1048	2.00
180	3.2227	3.3367	3.53	3.2912	2.12
190	3.4018	3.5288	3.73	3.4781	2.24
200	3.5808	3.7216	3.93	3.6654	2.36
210	3.7598	3.9151	4.12	3.8531	2.47
220	3.9389	4.1092	4.32	4.0412	2.59
230	4.1179	4.3041	4.52	4.2298	2.71
240	4.2970	4.4997	4.71	4.4187	2.83
250	4.4760	4.6960	4.91	4.6081	2.95
260	4.6550	4.8930	5.11	4.7980	3.06
270	4.8341	5.0907	5.30	4.9882	3.18
280	5.0131	5.2891	5.50	5.1789	3.30
290	5.1922	5.4882	5.70	5.3700	3.42
300	5.3712	5.6880	5.89	5.5615	3.54
310	5.5503	5.8885	6.09	5.7534	3.66
320	5.7293	6.0897	6.29	5.9458	3.77
330	5.9083	6.2916	6.48	6.1386	3.89
340	6.0874	6.4943	6.68	6.3318	4.01

Figure 8. The total T^2 contribution to ρ for K ($a = 5.223 \times 10^{-8}$ cm) in units of $10^{-8}\,\Omega$ m as a function of temperature.



ρ
6
5
4
3
2
1
2
3
90 110 130 150 170 190 210 230 250 270 290 310 330
T in °K
1 ρ_H plus the total T^2 contribution (PEA)
2 ρ_H plus the total T^2 contribution (TEA)
3 ρ_H
+ ρ (Exp.)

Table 15. The Cubic and Quartic Shift contributions to the phonon frequencies in units of 10^{12} c/s for the vector $\underset{\sim}{q}$ = (0.5,0.5,0.5)x2π/a and other vectors along the direction [1,1,0] in Na.

$\underset{\sim}{q}$ x (2π/a)		5 °K		90 °K		160 °K		296 °K		361 °K	
		TW	GT	TW	GT	TW	GT	TW	GT	TW	GT
(0.2,0.2,0.0)	L	0.028	-0.025	0.033	-0.035	0.078	-0.046	0.157	-0.074	-0.050	-0.092
	T1	0.042	-0.013	0.098	-0.062	0.231	-0.094	0.526	-0.134	1.280	-0.154
	T2	0.009	-0.013	-0.010	-0.030	0.007	-0.044	0.008	-0.082	-0.460	-0.093
(0.3,0.3,0.0)	L	0.038	-0.044	0.053	-0.050	0.098	-0.070	0.210	-0.133	0.130	-0.151
	T1	0.041	-0.015	0.105	-0.068	0.245	-0.107	0.579	-0.160	-1.140	-0.178
	T2	0.008	-0.023	-0.013	-0.040	-0.004	-0.054	-0.011	-0.084	-0.419	-0.101
(0.4,0.4,0.0)	L	0.046	-0.051	0.070	-0.070	0.129	-0.107	0.265	-0.187	0.261	-0.206
	T1	0.041	-0.017	0.114	-0.068	0.282	-0.102	0.656	-0.154	0.875	-0.167
	T2	0.008	-0.021	-0.095	-0.034	-0.003	-0.051	-0.012	-0.090	0.557	-0.103
(0.5,0.5,0.0)	L	0.050	-0.052	0.075	-0.059	0.137	-0.116	0.281	-0.204	0.619	-0.230
	T1	0.035	-0.021	0.104	-0.076	0.255	-0.093	0.596	-0.147	1.796	-0.162
	T2	0.012	-0.016	0.000	-0.038	0.012	-0.053	0.021	-0.109	0.489	-0.111
(0.5,0.5,0.5)	L	0.040	-0.040	0.066	-0.049	0.125	-0.072	0.257	-0.146	1.632	-0.190
	T1	0.040	-0.040	0.066	-0.049	0.125	-0.072	0.257	-0.146	1.632	-0.190
	T2	0.040	-0.040	0.066	-0.049	0.125	-0.072	0.257	-0.146	1.632	-0.190

L Longitudal mode

T Transverse mode

TW This work (QS)

GT Glyde and Taylor (1971) (CS)

Table 16. The Einstein phonon frequencies in units of 10^{13} c/s for Na and K

	ω_E	ω_E'
Na	1.671986	1.707663
K	1.025302	1.046742

7. CONCLUSION

We have numerically evaluated the contribution to ρ for Na and K from the Debye-Waller (DW), multi-phonon (MP) term and anharmonic contributions arising from the cubic and quartic shifts (CS and QS) of phonons, the phonon width (W) and the interference term, using a first principle approach (Shukla and Taylor (1976)). The third and fourth rank tensors arising in the anharmonic coefficient have been evaluated by the Ewald method (1921). The contribution to ρ from the DW and MP term and QS have been evaluated exactly and the contribution to ρ from the CS, QS, W and I term have been evaluated approximately in the partial and total Einstein approximations.
The numerical results obtained indicate a strong pairwise cancellation between: the DW and MP term, the QS and CS and the W and I term.
Hence we can conclude that the contribution to ρ from the BT^2 term in the high temperature limit is small.

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